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*Journal of the*
# Electrochemical Society

**FEBRUARY 1957** **VOL. 104 · NO. 2**

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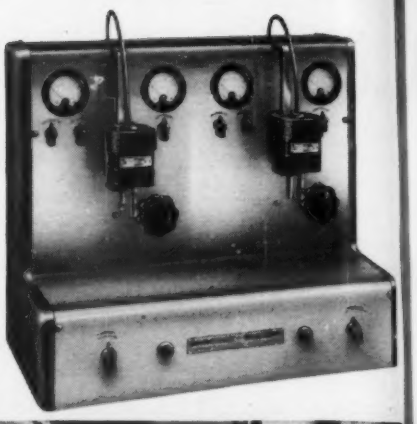

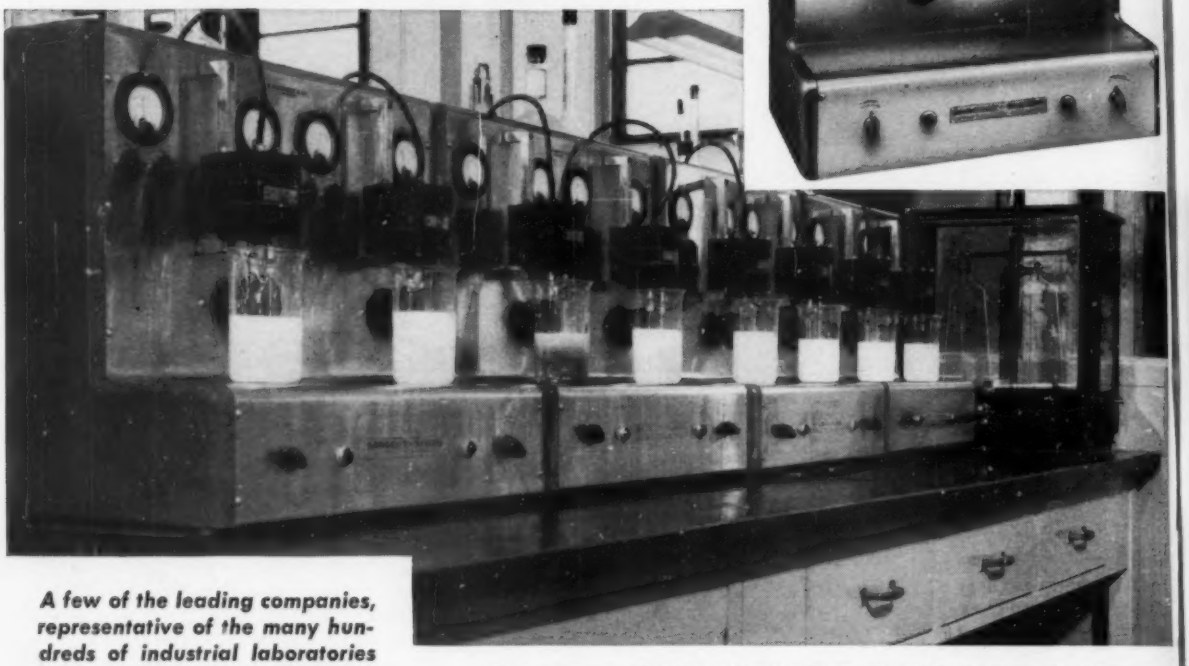

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# Editorial

## Safeguarding Science

*AS NEW PRODUCTS* result from advances in science there are new problems of production—witness the growth and machining of germanium crystals, the mechanisms for production line transport of cathode-ray tubes, and the remote controls for the handling of radioactive isotopes. But there are other problems which are brought about by scientific progress. One of great interest to the designer, and of importance to all of us, is the safeguarding of the public. While it is the duty of those who serve the public to do it safely, it is the special responsibility of those who devote their lives to this chosen work. It is not a narrow field, this scientific policing, but it is one of the broadest and in many ways most exciting branches of the technological advance of our modern society.

The inventor's part in a new product may involve one man or it may involve many men bound together in a great laboratory. The development and production of the product involves many workers, many helpers, and capital in the form of machines and buildings. Then we find a step that is of more importance with each passing year—the review of the product to see that it will be safe for use by the general public or in areas which are accessible to the public. This also involves many men with varied skills and with special laboratory testing facilities.

The problems are diverse. Will aluminum-coated steel corrode and permit hazardous spillage from gas vents used in residences? Will a plastic jacket prevent spontaneous implosion of a color television picture tube? If a child touches a farmer's electric fence on a rainy day will he be able to release himself? Does use of that new superefficient refrigerant expose the householder to toxic effects? Will deterioration of copper-plated electric heater reflectors cause ignition of the walls in which they are set? Will the operator of an x-ray type can filling inspection machine be exposed to a radiation hazard? How about the same problem when your boy watches a prize fight in a closed-circuit television theater? Will liquid sodium-potassium be retained in silver-soldered housings? Is lead a suitable container for cobalt 60 in case of a fire? If not, would uranium be satisfactory? Does copper deteriorate appreciably when operated at temperatures of 250°C? What harmful effects on building materials would there be if electrical wiring were operated at double its present temperature limits? What is the reason for cotton bale fires in freight cars since the railroads have gone over to diesel operation? Is that nurse's uniform a potential source of static discharge in the hospital operating room? What causes one design of fire extinguisher to corrode and become inoperative—why does another explode? Is it safe to increase the height of stacks of automobile tires in warehouses?

These and many other like questions have proved so intriguing to the engineers and scientists at safety testing laboratories that graduates who go there looking for experience find career jobs that give them a large measure of personal accomplishment and satisfaction. They are truly safeguarding the giant, forward steps of scientific progress.

—K. S. GEIGES[1]

[1]Chief Engineer, Underwriters Laboratories, Inc.

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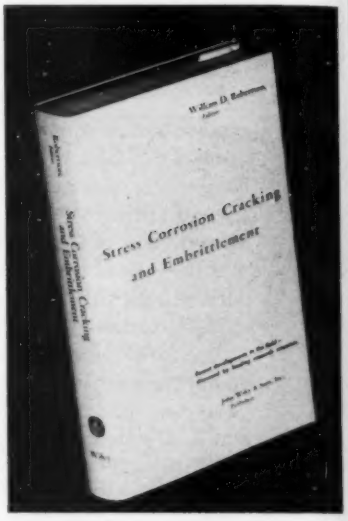


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The eighteen authorities who contributed to the work give extensive consideration to those aspects of the subject which affect the stability and safety of structures—which have increased in significance in recent years because of increasing loads and severity of operating conditions due to increased production, higher speeds, and higher temperatures of operation. The work includes papers from four countries, reflecting important work done in industry and in university laboratories.

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# Instrumentation for Use in Storage Battery Studies

G. W. Work and C. P. Wales

*Naval Research Laboratory, Washington, D. C.*

ABSTRACT

Instrumentation for use in a wide range of storage battery studies has been evolved. This storage battery analyzer features simplicity and accuracy of control, a wide scope of variables measured, and a complete, continuous record.

A null-balance servo system controls the output of the rectified d-c power supply at any desired current or voltage by continuously regulating the a-c input. Individual plate potentials, temperature, gas concentrations, and gas volumes are continuously measured and recorded. Optional equipment permits additional types of automatic cycling or other use in varied applications. The possibilities of the use of such methods are briefly illustrated and discussed from data on some Ni-Cd cells.

While many storage battery studies have been made in the past, much of the information has been difficult to interpret, at least partly because of the limited scope or type of measurements. The cell characteristics usually measured are voltage, current, and temperature, plus scattered observations of gas evolution, and, in the case of the Pb-acid battery, specific gravity of the electrolyte. Since each of these measured functions often includes several variables, the data may fail to indicate clearly where changes are taking place. The cell voltage, for example, is made up of the potential of both the positive plate and the negative plate. Since many factors affect each of these individually, cell voltage does not necessarily reflect the true picture. Individual plate potential measurements have often been made but seldom on a continuous basis. If the individual plate potentials are correlated with the gas evolution from that plate, the data become much more useful. In addition, data taken on a 24 hr/day basis, with such variables as current and temperature accurately controlled, would not only save time but might turn up unexpected yet important features.

In an attempt to obtain a more complete picture of an operating battery, a number of methods have been developed over the course of several years at this laboratory. More recently these methods have been incorporated into a single system which can be put into use and operated like any other laboratory instrument. This storage battery analyzer is simple to understand and use, and can, for the most part, be built from commercially available parts at a reasonable cost. Although the principles involved are not necessarily new, this analyzer's uniqueness lies chiefly in the combination of simplicity and accuracy of control, the scope of the variables measured, and the complete and continuous record obtained. While the equipment described is an outgrowth of work on alkaline storage batteries, it was so designed that it may be used with any other type of battery or with related problems.

## Basic Units

The instrumentation consists of three general groups of components: (*a*) the power supply, (*b*) the analyzer, and (*c*) the recorder. All components are mounted on a standard 19-in. relay rack in a single cabinet except for the large wet test meters and power units rated at 30 amp or more.

*Power supply group.*—The power supply group includes the main power unit, a controller unit, and a battery for a low-voltage d-c source.

The main power units are built in several sizes in the interest of efficiency. Beginning with a 60-cycle a-c supply in each case, a full-wave rectified DC with maximum ripple of 1% is obtained by means of a variable transformer, a copper oxide type of rectifier, and a filter circuit. The small to medium size units operate from a 115-v single-phase line as a matter of convenience. Three-phase AC would be preferred, if available, since it gives a better current characteristic with less filtering and has been used with all large power units. The unit also houses the appropriately sized charge-discharge current relays, shunts, current and voltage indicating meters, and terminals. The recorder shunt value is chosen so as to give an indication well up on the recorder scale and so that the recorder reading will be a simple multiple of the actual current. Control shunt sizes are chosen so that the 10-turn variable resistors are not operated at their extreme ends and may usually be selected for easy reading from the dial for presetting both charge and discharge values. Regardless of the size or rating, all power units have uniform plug-in connections to the recorder and the controller, and thus may be used interchangeably to meet the specific power need. Terminals are also provided for attaching an appropriately sized discharge resistor. This resistor is selected to give the discharge circuit a potential drop somewhat greater than the cell potential so that the power unit must add a little to drive the discharge at the desired rate. These discharge resistors range from small radio types to large water-cooled units. An unusual type in this latter group is a motor-driven variable resistor consisting of a pair of spirally wound brass tubes with graduated wall thickness. This construction gives the effect of a tapered rheostat with a resistance range which permits a 2 v battery to be discharged at rates between 50 and 1000 amp.

The heart of the controller unit is a servo-amplifier system operating on the null balance principle. From the wiring diagram, Fig. 1, it may be seen that the input sig-

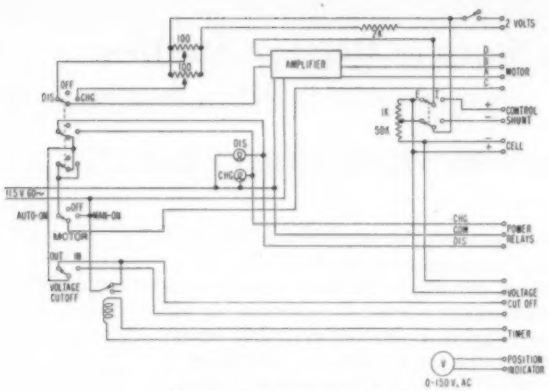


FIG. 1. Controller unit

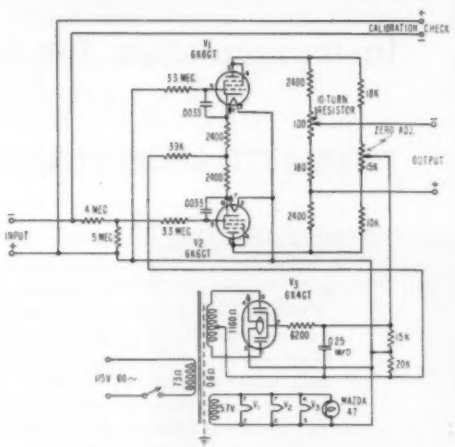


FIG. 2. Reference electrode unit

nal to the servo, taken from the control shunt (if current is to be controlled) or from a voltage divider (if voltage is to be controlled), is continuously compared with a standard millivoltage set by means of the 10-turn potentiometers, and powered by the 2 v Pb-acid cell. Any unbalance is converted to AC, amplified, and used to drive a two-phase induction motor geared to the variable transformer in the main power unit. Thus, the d-c output is continuously regulated by changing the a-c input to the rectifier. The controller unit also includes the necessary control switches, indicating lights, control knobs for setting the current or potential values for both charge and discharge, and a meter to indicate the position of the variable transformer. In addition there is space on the panel for insertion of a voltage cutoff unit. Although this controller has not been used for that purpose, there appears to be no reason why it could not regulate the output of a d-c generator, the servo motor being geared to the field rheostat.

The third part of the power supply group is a constant low-voltage d-c source, which is required to supply the bucking potential for the controller, power for the H analyzers, and, in some cases, power to the solenoid-operated gas volume marking pens. Suitable regulated electronic d-c sources are available but are expensive. A 2-v, 200-amp hr, low-discharge type of Pb-acid cell has been found quite satisfactory for the first two needs, and a small transformer-rectifier mounted on the recorder case is adequate for the recorder pens. Ideally, the H analyzers should have a constant current source, but, since the current can be recorded continuously for reference, this type of battery is adequate.

*Analyzer group.*—The reference-electrode unit plus an auxiliary electrode make possible continuous individual plate potential measurements. A Hg, $HgO/OH^-$ half cell with its tip in the electrolyte just above the tops of the plates has been found quite satisfactory as a third electrode with alkaline batteries. The indication is somewhat affected by the position of the electrode tip in the lines of force about the tops of the plates during current flow through the cell being measured. If the tip is kept in the same position, however, reproducible measurements of magnitude and direction of potential change can be made.

The electronic part of the reference-electrode unit converts the potential between the half-cell and one battery terminal to a continuously recordable signal without polarizing the half-cell. This unit serves as many as three reference electrodes and is basically the pertinent parts of three high-resistance electronic voltmeters modified and mounted on a single chassis. A voltmeter is modified by simply replacing a resistor ahead of the indicating meter with a voltage divider of the same total resistance and taking the output to the recorder from part of this new voltage divider. Fig. 2 is a circuit diagram of one such modified voltmeter. Provision is also made for periodic setting or checking of the calibration by plugging a portable potentiometer into the jacks on the front panel.

The H analyzer determines the concentration of H in the gas evolved from one to three cells at a time by means of commercially available, thermal-conductivity-type measuring cells. The degree of bridge unbalance and the current passing through the cells are both recorded. The analyzer is calibrated at three current values with several concentrations so that if the current varies, the gas concentration can still be determined from the recorded cell current. Any spray is removed, and the gas is dried by passing it over solid KOH before it reaches the analyzing cells. With the water vapor thus removed, oxygen may be calculated readily from the H record.

Gas volumes are measured by the use of the proper size of wet test meter. Commercial wet test meters are available in volumes of one liter or more and need no alteration other than the addition of an electrical contact to facilitate recording the revolutions on a time recorder. In this case, the revolutions may be recorded by pens, mounted on the side of the main recorder, which mark on the edge of the chart in line with the recorder printing. A 20-ml wet test meter for use with small cells or low gas flows has been designed and built along the same general principles as the larger types. Fig. 3 shows an exploded view of the plastic rotor which is the basic measuring element in this meter. The revolutions of the rotor are counted by an optical photocell system triggered by a small mirror on the rim of the rotor. Thus, knowing the volumes of gas recorded

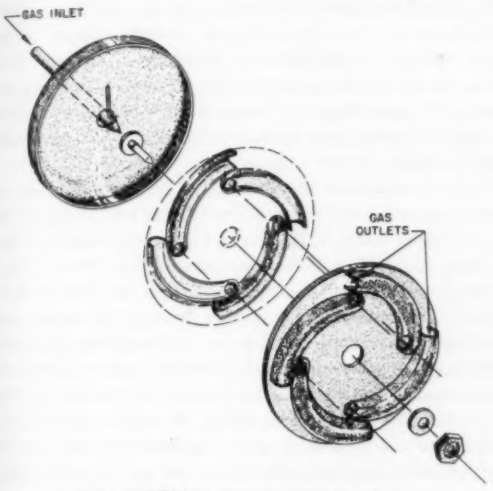


FIG. 3. Midget wet test meter rotor

against time and the gas concentration, H and oxygen gassing rates may be calculated.

Voltage dividers made from precision resistors are used to get recordable cell and/or battery voltages. Current values are obtained from appropriately sized shunts. Temperature measurements utilize the usual thermocouples. Using the measuring instruments in a temperature-controlled room simplifies gassing calculations, and another variable may be eliminated if the batteries being studied are in a temperature-controlled box.

*Recorder.*—Any standard, multipoint, strip chart, electronic, millivolt potentiometer which records continuously may be used to indicate and record data provided its selector switch is fully nonshorting between adjacent points. Staggering the points on the switch not only makes chart reading easier but also helps prevent trouble from high voltages between leads from opposite ends of a battery. The instrument most commonly used at this laboratory is a 16-point, 0–20 mv, self-balancing recorder with a choice of several chart speeds. It prints the sequence of points in about 2½ min, although this may be speeded up when desired. The three-pen, gas-volume marking equipment often used at the right side of the recorder paper was designed and built at this laboratory, but one or two pen units are available as part of the recorder from some manufacturers.

## Optional Equipment

*Voltage cutoff.*—Control points are available for installation on some recorders. When so equipped, the recorder checks certain points each time they are measured, and if the value has reached an adjustable, pre-set upper or lower limit, a switch is operated automatically to open or close a circuit. If the cell voltage, for example, is connected to one of these control points, it may be used as an automatic voltage cutoff to end a charge or discharge.

For recorders not equipped with control points, a voltage cutoff unit may be added to the basic controller unit. This cutoff unit consists of a voltage-sensitive relay with built-in solenoid reset, an adjustable series resistor, and a small relay wired into the basic controller at the point indicated in Fig. 1.

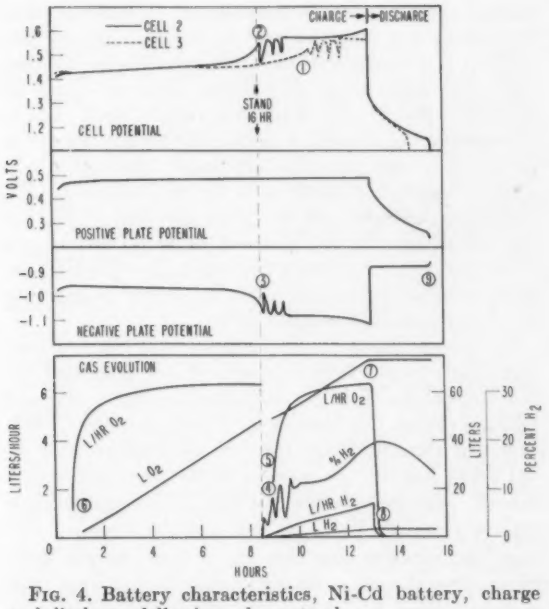


FIG. 4. Battery characteristics, Ni-Cd battery, charge and discharge following a long stand.

*Cycler.*—The basic controller has provision for starting, stopping, or delaying an operation by means of an external timer. Where automatic cycling is desired, the functions of the CHG-OFF-DIS switch are transferred to a pair of interlocking relays. The original CHG-OFF-DIS switch or a single-pole, double-throw, three-position switch then operates the relays during manual operation and a single-pole, double-throw timer operates them during cycling.

Another type of cycle to which the controller may be adapted is a cycle lasting a definite length of time but with both charge and discharge cutoff on voltage. Some AgO-Zn cells, for example, discharged at 10 amp to 1 v, immediately recharged at 4 amp to 2.1 v, and stood the remainder of 48 hr before automatically repeating the cycle.

A somewhat more common cycle is one where the charge is against time and the discharge is to a voltage. This is readily accomplished with the controller to which a voltage cutoff has been added with a minor wiring change to include a time-delay relay. This latter relay resets the voltage cutoff at the start of the charges.

## Applications

Data from a Ni-Cd battery cycle may be used to illustrate one type of study made possible by the instrumentation and techniques described. In this cycle, cell voltage was measured on all four cells of the battery and, in addition, individual plate potential and gas evolution measurements were made on two of the cells.

In Fig. 4, data from one cell in each pair have been replotted from the recorder chart for easier reading. The voltage rise on cell 3 during the charge was slower than would be anticipated, but it appeared to be otherwise

normal until it began to fluctuate at ①. Although this fluctuation was found on two of the four cells in this cycle, it is not characteristic of a normal charge. Lacking any other information, this erratic behavior might be confused with a bad electrical connection or breakdown of a measuring component. A similar fluctuation appears at ② on cell 2, but, from the additional data taken, it is obvious that the fluctuations in the cell voltage are due to fluctuations in the negative plate potential ③, and are also reflected in the H concentration at ④. The volume of the gas meter per revolution was large enough to obscure a similar fluctuation appearing in the gassing rate at ⑤, but it was undoubtedly there.

Gas measurements ⑥ also indicate that gas evolution began early in the charge for cell 2. This suggests that the cell was either not deeply discharged or that it was not taking a charge. Calculations from the gas record ⑦ indicate that the net charge put into the positive plate of cell 2 was, however, about equal to the rated capacity of the cell. This would be the maximum, since positive plate capacity normally limits the cell capacity. In sharp contrast, the negative plate appears to have charged quite efficiently with only a limited amount of H having been evolved during the charge ⑧. When the charge was stopped, over twice the rated capacity of the cell appears to have been put into the negative plate; yet the lack of H evolution showed it was far from being fully charged. Furthermore, the negative plate potential began to drop near the end of the following discharge ⑨ in spite of the long charge. All this suggests that the self-discharge rate of the Cd plate was high under these conditions of stand and that there was a high ratio of negative plate to positive plate capacity in this battery.

More recent work on similar cells indicates that the apparent amount of charge taken by the Cd plate was not necessarily related to the true capacity. Gas measurements during stand show that the gassing rate of the Ni-Cd battery dropped off rapidly during the first few hours of stand. This lack of gas evolution does not mean that self-discharge had stopped, however, for residual discharges following stands indicate appreciably more capacity loss than could be accounted for by the evolved gas. While the cell characteristics were being observed on a 24 hr/day basis, the cell actually began to absorb oxygen from the atmosphere; this oxygen in turn oxidized the Cd plate.

Thus, it is sometimes possible to pick up and interpret unexpected characteristics from the detailed measurements on a 24 hr/day basis. A permanent record is also available for future evaluation in the light of later developments.

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# Thermogalvanic Potentials and Currents at Aluminum Surfaces in Industrial Water

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ABSTRACT

Potentials and galvanic currents at 28 Al surfaces in Columbia River water were studied between room temperature and 100°C. The Al potential changed by approximately 0.6 v over this interval, becoming more anodic with increase in temperature. Similar but somewhat smaller changes in potential were noted in buffer solutions.

By coupling identical Al samples, one at 100° and the other at room temperature, a maximum current density of 40 μamp/cm² was maintained.

During a study of the corrosion of Al in Columbia River water, an appraisal of possible thermogalvanic potentials and currents was undertaken.

In certain other systems, thermogalvanic effects of an appreciable order of magnitude have been observed. For example, Carr and Bonilla (1) found that a heated Ni electrode is anodic to its cooler counterpart. Similar results were reported by Uhlig and Noss (2) for Fe corrosion. Berry (3) found that Cu behaved in the opposite sense: a cold Cu electrode was anodic to a warmer one.

Only two references to the temperature coefficient of the Al electrode were found in the literature (4, 5). In both cases, a heated specimen of Al was anodic to a similar cooler specimen, but, as the determinations were made in fairly concentrated salt solutions, the results are not necessarily applicable to industrial water.

No quantitative predictions of thermogalvanic effects could be deduced from physical theory. The Thomson effect, a measure of the difference in potential between two areas of unequal temperature in a metal object, could not be used even qualitatively for Al, because of uncertainties in existing data (6). An analytical expression for the difference in electrical potential congruent with a difference in temperature between two points on a metal surface is afforded by the Fermi-Dirac statistics (7), but

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no provision is made for possible electrolytic effects if the surface is immersed in a liquid.

An attempt by Jahn (8) to show that the Gibbs-Helmholtz equation applies to single electrode potentials is of doubtful validity, since at least two fundamental assumptions are involved: (*a*) that the temperature coefficient of a reference electrode may be determined, and (*b*) that the Nernst equation applies to the electrode under investigation. The first assumption is discussed by Lewis and Randall (9) and by Clark (10). In a more recent paper, Buffington (11) calculated that the temperature coefficient of the H electrode was −0.91 mv/°C, the minus sign indicating that the potential becomes more noble with increasing temperature. Combining this value with other thermodynamic data, Buffington computed a table of temperature coefficients for the electrode potentials of a number of metals. For Al, his estimate was −1.45 mv/°C, indicating a decrease in anodic tendency with increasing temperature. This result differs in algebraic sign from that reported in the previously cited papers (4, 5).

A specimen of Al immersed in a natural water is, of course, fundamentally different from a standard Al electrode. Not only is the water substantially free from Al ions; it is also within a range of *p*H incompatible with appreciable concentrations of Al in cationic form. Under such conditions the Nernst equation is inapplicable, either as originally derived or in the more sophisticated forms proposed by Butler (12) and by Gurney (13). In fact, the potential of an Al electrode in an aqueous solution within the *p*H range 5.5–7.5 lies near the bottom of a roughly U-shaped curve (14), and is extraordinarily sensitive to changes in acidity or alkalinity but not appreciably responsive to changes in concentration of Al ions.

An equation for the electrode potential of a metal dissolving in a solution practically free from its own ions has been derived by Glasstone, Laidler, and Eyring (15) in a form containing kinetic constants for which the temperature coefficients are not readily evaluated.

In view of these considerations, it is perhaps more realistic to abandon the concept of a reversible electrode, and to consider the metal to form not Al ions, but $Al_2O_3 \cdot 3H_2O$, which, according to Draley and Ruther (16), has been identified by x-ray diffraction methods on a corroding Al surface.

Writing the equation in terms of the observed phase:

$$2Al + 6H_2O \rightarrow Al_2O_3 \cdot 3H_2O + 3H_2$$

the standard free energy change can be calculated from the entropies of the reactants and products. From Kelley's monograph (17), the pertinent entropies at 25° are: Al, 6.77; $Al_2O_3 \cdot 3H_2O$, 33.5; $H_2$, 31.3; $H_2O$, 16.75.

The entropy change for the reaction is therefore 13.4 e.u., and the temperature coefficient, −13.4 cal/°C. The tendency for Al to react with water therefore increases with increase in temperature in the vicinity of 25°.

The course of the reaction is undoubtedly affected by the type of oxide film initially present on the Al. Samples were therefore tested with factory finish in order to evaluate the type of surface on the Al actually in use.

## Experimental

*Potentials in Columbia River water.*[2]—Six 2S Al cans were immersed in a beaker of treated Columbia River water through which the rate of flow was 500 cc/hr. The cans were protected at the air-water interfaces by a coat of Tygon paint, leaving approximately 60 cm² of Al surface exposed to the water. Potentials of the cans were measured by comparison with a Beckman calomel electrode at room temperature at intervals during a 3-hr period in order to establish a basis of reference and to observe any variations in potential with time. Two of the cans were maintained in water at room temperature as controls during a further interval of 210 min, during which the remaining four cans were slowly heated in the beaker of flowing water. Potentials of the cans were measured throughout the experiment, as shown in Table I. Values of the electrode potentials are recalculated to the H electrode scale, correcting for the temperature coefficient of the calomel electrode. The difference in potential between hot and cold specimens was of the order of 0.6 v.

The *p*H of the exit hot water was observed to have risen from 7.4 to about 8.5 as measured at room temperature, presumably because of the decomposition of bicarbonate and expulsion of carbonic acid. The change in alkalinity was considered to be a possible contributing factor to the change in potential of the Al, hence a suitably buffered substitute for the river water was sought. Obvious requirements for a suitable solution were believed to be freedom from bicarbonates and extraneous salts, and a low enough permanent hardness to avoid precipitation of scale on Al during heating.

*Potentials in simulated bicarbonate-free industrial water.*—A solution containing 1 g $CaSO_4$/l was considered to be typical of a simulated bicarbonate-free natural water. Duplicate cans were heated in this solution as in the preceding experiment with two similar cans held in reserve in cold solution. A decrease in potential of 0.5 was noted, as recorded in Table II. During the experiment, potentials of the control cans changed by about 0.12 v, hence the net potential difference was approximately 0.4 v. The *p*H of the solution was 7.2 at the end of the experiment, indicating that a closer control of the *p*H does not eliminate the temperature coefficient of the electrode potential of Al observed during heating.

*Potentials in 0.01M acetate buffer solution.*—As a further expedient to confine the change in *p*H observed during heating within narrower limits, a series of 0.01*M* acetate solutions of initial *p*H 5.0, 5.5, 6.0, 6.5, 7.0, and 7.5 were substituted for the simulated industrial water. Admittedly, a difference in film characteristics should be obtained, but a marked change in the electrode potential of the underlying Al would not be expected as a result of the substitution of acetate for sulfate ion. Al cans were heated in the buffer solutions in the same manner as in the previous cases. Portions of the solution were removed periodically and cooled for *p*H determinations. Measured *p*H values were constant within 0.1 unit throughout all of

[2] Composition of Columbia River water (ppm): $SO_4$, 11; Mg, 4.2; $SiO_2$, 5.3; $PO_4$, 0.021; Mn, 0.008; Cl, 0.5; Na, 2.0; Ca, 21. Soap hardness, 69. Alkalinity: phenolphthalein, 0.5; methyl orange, 58. Specific resistance, 4,000 ohm-cm.

TABLE I. *Potentials of 2S* Al *in Columbia River water*
Flow rate, 500 cc/hr; convention: Std. H electrode scale (v)
(*a*) Room temperature

| Time, min. | 0 | 30 | 60 | 90 | 120 | 150 | 180 |
|---|---|---|---|---|---|---|---|
| Specimen 1 | −0.13 | −0.13 | −0.20 | −0.29 | −0.35 | −0.36 | −0.37 |
| 2 | −0.13 | −0.17 | −0.19 | −0.24 | −0.29 | −0.30 | −0.33 |
| 3 | −0.13 | −0.12 | −0.21 | −0.29 | −0.35 | −0.36 | −0.36 |
| 4 | −0.15 | −0.14 | −0.19 | −0.26 | −0.30 | −0.31 | −0.33 |
| Control 1 | −0.14 | −0.14 | −0.14 | −0.21 | −0.27 | −0.32 | −0.36 |
| 2 | −0.15 | −0.15 | −0.21 | −0.27 | −0.35 | −0.39 | −0.41 |

(*b*) Increasing temperatures

| Time, min.<br>Temp, °C | 240<br>38 | 270<br>55 | 300<br>80 | 345<br>90 | 350<br>92 | 380<br>96 | 385<br>98 | 390<br>98 |
|---|---|---|---|---|---|---|---|---|
| Specimen 1 | −0.50 | −0.52 | −0.53 | −0.60 | −0.61 | −0.67 | −0.82 | −0.85 |
| 2 | −0.50 | −0.52 | −0.53 | −0.61 | −0.63 | −0.69 | −0.80 | −0.85 |
| 3 | −0.51 | −0.52 | −0.53 | −0.65 | −0.69 | −0.70 | −0.85 | −0.88 |
| 4 | −0.48 | −0.51 | −0.52 | −0.64 | −0.70 | −0.75 | −0.85 | −0.93 |
| Control 1 | Maintained at room temperature | | | | | | | −0.19 |
| 2 | | | | | | | | −0.24 |

TABLE II. *Potential of 2S* Al *in* $CaSO_4$ *Solution (1 g/l)*
Voltages recalculated to standard $H_2$ electrode

| Time (min).<br>Temp, °C<br>*p*H | 0<br>Room temperature<br>6.15 | 15<br><br>6.13 | 30<br><br>6.10 | 45<br><br>6.09 | 60<br><br>6.09 | 75<br><br>6.12 | 90<br><br>6.15 | 105<br><br>6.20 | 210<br><br>6.21 |
|---|---|---|---|---|---|---|---|---|---|
| Specimen 1 | −0.06 | −0.06 | −0.06 | −0.06 | −0.06 | −0.07 | −0.09 | −0.10 | −0.12 |
| 2 | −0.11 | −0.11 | −0.11 | −0.11 | −0.12 | −0.12 | −0.12 | −0.13 | −0.14 |
| Control 1 | −0.11 | −0.12 | −0.08 | −0.09 | −0.13 | −0.12 | −0.12 | −0.12 | −0.12 |
| Control 2 | −0.08 | −0.08 | −0.06 | −0.06 | −0.09 | −0.08 | −0.19 | −0.09 | −0.10 |

| Time<br>Temp, °C<br>*p*H | 135<br>44<br>6.33 | 150<br>48<br>6.41 | 165<br>51<br>6.45 | 180<br>55<br>6.52 | 195<br>59<br>6.58 | 210<br>61<br>6.61 | 225<br>62<br>6.65 | 240<br>69<br>6.78 |
|---|---|---|---|---|---|---|---|---|
| Specimen 1 | −0.18 | −0.18 | −0.18 | −0.18 | −0.19 | −0.25 | −0.22 | −0.21 |
| 2 | −0.20 | −0.22 | −0.22 | −0.29 | −0.23 | −0.24 | −0.26 | −0.38 |

| Time<br>Temp, °C<br>*p*H | 255<br>70<br>6.86 | 270<br>73<br>6.95 | 285<br>82<br>7.10 | 300<br>85<br>7.22 | 315<br>91<br>7.25 | 330<br>95<br>7.32 | 345<br>97<br>7.30 | 360<br>97<br>7.20 |
|---|---|---|---|---|---|---|---|---|
| Specimen 1 | −0.42 | −0.51 | −0.64 | −0.64 | −0.66 | −0.67 | −0.66 | −0.65 |
| Specimen 2 | −0.45 | −0.56 | −0.66 | −0.65 | −0.67 | −0.67 | −0.67 | −0.66 |
| Control 1 | Maintained at room temperature | | | | | | | −0.26 |
| Control 2 | | | | | | | | −0.26 |

TABLE III. *Potential of 2S* Al *in acetate buffer solutions at various temperatures*
Voltages recalculated to standard H scale at 25°C

| Initial *p*H* | 5.0 | | 5.5 | | 6.0 | | 6.5 | | 7.0 | | 7.5 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Potential at room temp | −0.15 | −0.10 | −0.16 | −0.24 | −0.26 | −0.27 | −0.17 | −0.17 | −0.06 | −0.11 | −0.10 | −0.15 |
| Potential at 99°C | −0.38 | −0.35 | −0.83 | −0.79 | −0.75 | −0.78 | −0.72 | −0.74 | −0.82 | −0.65 | −0.70 | −0.72 |
| Potential after cooling at room temp | | | −0.26 | −0.26 | −0.25 | −0.10 | −0.26 | −0.07 | | | | |
| Duration of experiment, min. | 165 | | 180 | | 270 | | 270 | | 345 | | 420 | |

All *p*H determinations were made on portions of solution cooled to room temperature.
* Value of *p*H constant within +0.1 unit through experiment.

TABLE IV. *Thermogalvanic currents*

Concentric cylindrical electrodes, approx. 45 cm² area.
Cold electrode at 20°.
Hot electrode temperature as noted.
Gas bubbling through cell.

| None | | Nitrogen | | Oxygen | |
|---|---|---|---|---|---|
| Temp, °C | Current (μamp) | Temp, °C | Current (μamp) | Temp, °C | Current (μamp) |
| 67 | 44 | 70 | 30 | 65 | 30 |
| 75 | 56 | 75 | 50 | 69 | 36 |
| 76 | 72 | 76 | 60 | 73 | 40 |
| 84 | 136 | 77 | 80 | 90 | 50 |
| 92 | 250 | 85 | 120 | 97 | 250 |
| 93 | 320 | 86 | 140 | 98 | 350 |
| 94 | 420 | 88 | 154 | 99 | 490 |
| 98 | 600 | 92 | 160 | 99.5 | 600 |
| 99 | 720 | 99.5 | 180 | 100 | 640 |
| 100 | 860 | 100 | 220 | | |
| Maximum C.D., anodic, amp/cm² | | | | | |
| $1.9 \times 10^{-5}$ | | $4.9 \times 10^{-6}$ | | $1.4 \times 10^{-5}$ | |

the heating intervals. The Al became more anodic in all cases, as shown in Table III.

*Galvanic currents between hot and cold specimens of* Al *in Columbia River water.*—Potential differences reported in the preceding section were obtained by open-circuit measurements. There remained a need to determine whether a measurable current might be maintained between two similar Al surfaces at widely different temperatures when immersed in water.

An electrolytic cell was assembled, consisting of an Al can approximately 5 cm in diameter and 20 cm deep, and a sheet of Al obtained by shearing open a similar can. The upper ends of facing surfaces were painted with Tygon, leaving exposed surface areas of approximately 45 cm². The sheet of Al was bent to conform to the cylindrical can, leaving a clearance of approximately 2 mm around the intact can. The electrodes were mounted in a beaker through which Columbia River water was passed at a rate of 12 l/min. The can was provided with a rubber stopper containing a thermometer and inlet and outlet tubes, through which (*a*) hot water and (*b*) steam were passed. Temperatures up to 100° were readily maintained inside the heated electrode. The electrodes were connected through an external resistance of 1000 ohms and a microammeter.

(*A*) The galvanic current was small, of the order of only a few microamperes, until the temperature of the can reached about 60°C. From this point, the current increased rapidly with rising temperature to 860 μamp. Agitation with N served to lower the current by an appreciable amount, whereas the effect of a stream of oxygen was less marked (Table IV).

(*B*) The temperature of the can was held at 100° by a current of steam for 75 hr. The current was fairly constant at 1.8 ma throughout the experiment, corresponding to an average anodic current density of approximately $4 \times 10^{-5}$ amp/cm².

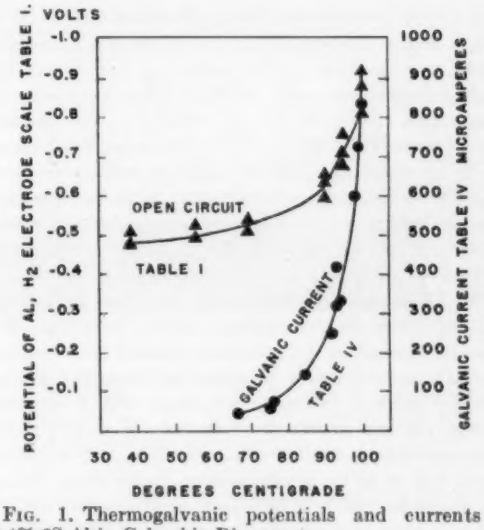


FIG. 1. Thermogalvanic potentials and currents o 99.4% 2S Al in Columbia River water.

## DISCUSSION

### *Potentials in Columbia River Water*

A comparison of potentials obtained at 100° with those of the control samples at room temperature is sufficient evidence that the differences in potential cannot be explained on the basis of time-dependency. The abrupt changes in potential indicate a mechanism unrelated to a simple temperature coefficient. It is more probable that the effects are related to film impairment.

The exact role played by the oxide film in depressing the electrode potential of Al has been the subject of much speculation and many ingenious explanations (18). Any operation that removes a portion of this film enhances the apparent "solution potential" of the metal (19). The results of Brown and Mears (20) show that the potential of Al becomes more anodic as the film is progressively scratched. A potential difference of 0.32 v was noted between the potentials of an unscratched coupon and one scratched by a standard procedure.

If the integrity of the hydrated oxide film is indeed the chief factor governing the magnitude of the observed electrode potential, the marked change above 90° might be attributed to an accelerated deterioration of this film. According to data of Draley and Ruther (16), the corrosion product undergoes a transition from $\beta$-$Al_2O_3 \cdot 3H_2O$ to $\alpha$-$Al_2O_3 \cdot H_2O$ in approximately this temperature region. Accompanying the phase transition, there is undoubtedly widespread impairment of the protective film on the Al surface, so that unprotected metal is exposed as effectively as if it were scratched mechanically, as for instance by the technique of Brown and Mears.

### *Galvanic Currents*

It was not feasible to make simultaneous measurements of open-circuit potentials and galvanic currents with the same specimens. By plotting the data of Tables I and IV on the same graph (Fig. 1), however, a significant correlation is evident. In the temperature range 40°–70°, the

open-circuit potential was fairly constant at $-0.50 \pm 0.02$ v. Within the same range the galvanic cell measurements were very low, of the order of 1 $\mu$amp/cm$^2$. The gradual slope of the open-circuit potential curve over the temperature range 70°–90° is reflected in the galvanic current curve. From 90° to 100° the potential became more anodic by about 0.2 v, and the galvanic current increased from 220 to 860 $\mu$amp, corresponding to an increase from 5 to nearly 20 $\mu$amp/cm$^2$. For the duration of the experiment, at least, the slope of the galvanic current curve kept pace with that of the potential curve.

The 75 hr experiment demonstrated that the current was not stifled by polarization or film formation. The constant current of 1.8 ma corresponded to a current density of approximately 40 $\mu$amp/cm$^2$ of anode surface.

If this galvanic current is associated with a corrosion process, the rate of attack of the anodic surface under these conditions is readily calculated. One $\mu$amp is equivalent to $3.35 \times 10^{-7}$ g Al attacked/hr. In the steam-heated cell, therefore, the rate of attack equivalent to the observed current was, for the duration of the experiment, $1.35 \times 10^{-5}$ g/cm$^2$hr. From these data, it may be concluded that the observed galvanic current represented a serious corrosion hazard unless curbed by an inhibitor.

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# Metallographic Study of Electroplated Coatings of Chromium and Nickel on Molybdenum

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ABSTRACT

Single-layer and multiple-layer coatings of electroplated Ni and Cr on Mo were studied metallographically to determine why these coatings failed when heated in air. In single-layer coatings, Cr was less subject to bonding failure than Ni and afforded better protection against oxidation. Cracking of Cr coatings was probably a major cause of failure, but good protection by Cr was possible if a layer of Cr-Mo alloy was developed at the interface. Multiple-layer coatings of Cr and Ni in which Cr formed the initial layer may be superior to single-layer coatings, but formation of blisters between the layers of Cr and Ni was a major cause of failure of this type of coating.

Because of its outstanding mechanical properties, Mo is attractive for use in construction of parts that must function at high temperatures; however, a serious drawback to its use is its very high oxidation rate above 700°C.

Many coatings have been developed which show good promise of preventing this oxidation. Prominent among elements used for this purpose are Si, Cr, Ni, B, Al, and combinations of these elements. Some of the most protective of these coatings are brittle, and they are damaged if the coated part is deformed. Furthermore, many po-

tentially effective coatings can be applied only by heating the Mo to very high temperatures, e.g., by painting and sintering, flame spraying and sintering, vapor plating, metallizing, etc. Many of these coatings can be applied effectively only above the recrystallization temperature of cold-worked Mo (900°–1100°C) or potentially useful Mo alloys (1100°–1300°C). Since the mechanical properties of recrystallized Mo are inferior to those of the cold-worked metal, it should be coated and used below the recrystallization temperature (1, 2).

Electroplating is of interest because it is a method of applying protective coatings at low temperatures. Metals such as Cr and Ni are of interest because they are oxidation-resistant metals that can be electrodeposited readily. Cr is of particular interest because it is soluble in Mo and does not form brittle intermetallic compounds, and because it has low thermal expansion, similar to that of Mo (Table I). Ni is of interest because it has relatively good resistance to oxidation by atmospheres containing $MoO_3$ (3), and because it has very high ductility. Ni forms brittle intermetallic compounds with Mo, however. Ni also has relatively high thermal expansion.

Electroplated coatings of Cr and Ni on Mo were very effective in protecting Mo from oxidation; however, they did not produce consistent results. A solution to the problem of protecting Mo, therefore, appears to depend more on finding the causes of failure of the more promising coatings than on finding new or different types of coatings that may be used.

The protective value of any coating on Mo is limited to that of its poorest area. This is uncommonly true for Mo because a body of Mo can be oxidized and completely distilled at an amazingly rapid rate through even the minutest flaw in the protective coating.

It was because of this characteristic that a metallographic study of protective coatings on Mo was made. The primary purpose of this study was to determine some of the probable causes of failure. For this reason, many of the areas examined were those containing defects or those suspected of containing defects.

## Procedures

*Plating.*—Standartl plating procedures for Cr and Ni were generally effective when Mo was properly cleaned. Plating procedures similar to those used at Battelle were described by Korbelak (4).

Most of the samples included in this study were prepared for plating by etching in HF, but some were prepared by etching in alkaline ferrocyanide. This latter method now is generally preferred to the acid etch, but both methods appear to be effective.

Cr plating was done in a chromic acid bath, and both hard Cr and low contraction Cr plates were deposited and examined. Except where noted, all Cr plates were low contraction Cr.

Ni plating was from a Watts-type bath, but it was necessary to employ a Ni strike prior to plating in order to obtain a good bond. A high-chloride Ni strike bath was used.

*Testing.*—Most of the specimens plated and tested consisted of 5- to 6-in. lengths of 80-mil rod. Some flat specimens about $\frac{1}{4}$ in. wide and about $\frac{1}{20}$ in. thick also were tested.

TABLE I. *Coefficients of linear thermal expansion near 20°C*

| Metal | Micro-Inches/°C. |
|---|---|
| Mo | 4.9 |
| Cr | 6.2 |
| Ni | 13.3 |

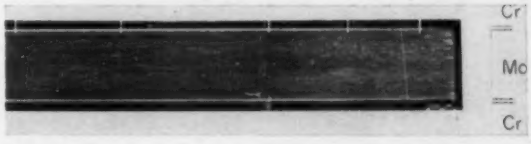


Fig. 1. Longitudinal section of 80-mil Mo rod electroplated with low-contraction Cr after 1077 hr at 900°C. Enlarged views of sections indicated are shown in Fig. 2. 10× before reduction for publication.

The coated specimens were tested in air by clamping them between water-cooled electrodes and applying sufficient electrical current to bring the temperature of the central portion up to the desired level. Most of the specimens were tested at 900°C, which was estimated to be about the maximum temperature to which cold-worked Mo could be heated without danger of recrystallization.

Temperatures were read with an optical pyrometer and were corrected for emissivity on the basis of an assumed value of 0.4.

Many of the specimens were removed before the protective coatings failed, but some of them were tested to destruction. Specimens that failed interrupted the current to an electrical timer so that testing time was automatically recorded in all cases.

Specimens tested in the above manner contained areas at all temperatures from room temperature to the maximum testing temperature. Because of this, it was possible to examine the structural changes at all intermediate temperatures for the period of time of any given test.

*Metallography.*—The metallographic procedures used were selected primarily for the purpose of revealing the crystalline structure of Mo. Specimens were first polished with a slurry of $Al_2O_3$ and chromic acid with heavy pressure on a fast wheel. A final short polish with light pressure was given with $Al_2O_3$ but without the chromic acid. Polished specimens were etched with Murakami's reagent. This procedure did not reveal the crystalline structure of the electroplated metal, but it did show the condition of this metal and revealed different phases in the coating.

## Metallographic Structures

Fig. 1 shows a photomicrograph of a section of 80-mil rod plated with about 3 mils of low-contraction Cr. This specimen was held at 900°C for 1077 hr. The left end of the section was at room temperature, the right end at 900°C. As may be observed, recrystallization of Mo occurred in the high-temperature zone of the specimen. Enlarged views of five sections of this specimen from left

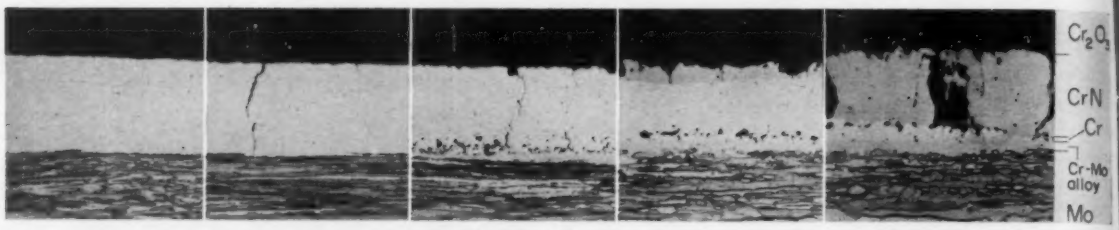


FIG. 2. Low-contraction Cr on Mo: section A, outside of heated zone; section B, inside heated zone; section C, inside heated zone; section D, inside heated zone; section E, after 1088 hr in air at 900°C. 250× before reduction for publication.

TABLE II. *Effect of different types of plate and of heat treatment in* H *on the lives of specimens of* Mo *electroplated with 3 mils of* Cr

| Type of Cr plate | Life in air at 900°C, hr |
|---|---|
| Low contraction | 300 |
| Low contraction, heat treated | 200 |
| Hard | 240 |
| Hard, heat treated | 50 |

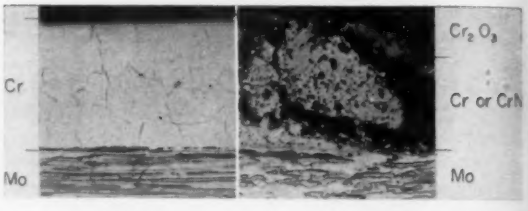


FIG. 3. Hard Cr on Mo: section A, outside heated zone; section B, after 1077 hr in air at 900°C. 250× before reduction for publication.

to right, as indicated by the markers of Fig. 1, are shown in Fig. 2.

Fig. 2A, which is a section outside of the heated zone that is under the water-cooled electrode, shows the Cr plate to be nonporous, well-bonded plating. Section B shows this plating in a zone heated only to moderate temperature, well below red heat. Severe cracking is apparent. Cracking is also apparent in section C. In this zone, there is evidence of some alloying of the Cr plate and the Mo base. Under the microscope, the dark areas of section C appeared to be voids. It also may be noted that very slight recrystallization of Mo is apparent in this area. The layer of Cr-Mo alloy also is evident in section D, and it is of interest to note that it apparently is little greater in thickness than it was in the lower temperature zone shown in section C. Some chromium oxide on the outer surface of the plating is barely apparent in this section. The structure of this material, however, does not indicate that it afforded much protection to the underlying metal. Evident also is an additional phase under the chromium oxide layer which apparently is CrN. The formation of a nitride layer under the oxide layer on Cr plate heated in air was described by Snavely and Faust (5).

Section E shows the structure of the Cr plate at the zone of maximum temperature, i.e., 900°C. Of particular interest in this section is the indication that only the Cr-Mo layer would appear to afford protection to the body of Mo. This layer, which apparently is less than 1 mil in thickness, is only slightly thicker than it was in zones of lower temperature. The indication that the thickness of the Cr-Mo layer is not highly time and temperature dependent under the conditions employed in this work was further supported by the structure of Cr-plated Mo after being heated to 1500°C in air. The Cr-Mo alloy layer on one specimen heated for 45 hr at 1500°C was about the same thickness as that on another specimen heated only 12 hr at 1500°C, and both were approximately the same as that of the specimen heated over 1000 hr at 900°C.

Because of the apparently protective nature of the layer of Cr-Mo alloy, it would appear desirable to preheat plated Mo in a nonoxidizing atmosphere, such as H, to develop the alloy layer before the specimen is heated in air. Such a procedure did not appear to improve the effectiveness of Cr plate, however, as is indicated by the results in Table II. Specimens tested were strips of Cr-plated Mo sheet $\frac{1}{2}$ in. wide by $\frac{1}{16}$ in. thick. Both low contraction and hard Cr were tested and one specimen of each type of plating was heated in H at 900°C for 72 hr prior to testing.

While flat specimens of Mo plated with Cr did not last more than a few hundred hours in air at 900°C, specimens of 80-mil rod plated with either low contraction or hard Cr were still good after 1000 hr under these conditions. The appearance of the low-contraction Cr after heating in air is shown in Fig. 1 and 2. The appearance of a similar sample plated with hard Cr is shown in Section A of Fig. 3. The porous nature of this type of plated metal is evident. The appearance of this plate after 1077 hr at 900°C is shown in Section B of Fig. 3. The Cr-Mo alloy layer, which was characteristic of the low-contraction Cr after heating, is not apparent in this figure. While this plating afforded better protection than was expected, it appears from Fig. 3 that its probable life at this temperature would be less than that of low-contraction Cr after similar treatment as was shown in Fig. 2.

Fig. 4 shows a specimen of 80-mil rod plated with about 3 mils of Ni. This specimen failed after 574 hr at 900°C. No general recrystallization of Mo is apparent in the zone of highest temperature except for a central zone which probably became very hot shortly before complete failure occurred.

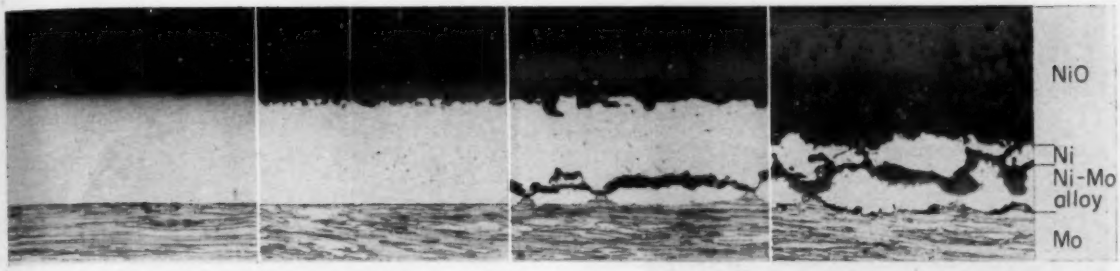


FIG. 4. Ni on Mo: section A, outside heated zone; section B, inside heated zone; section C, inside heated zone; Section D, after 574 hr in air at 900°C. 250× before reduction for publication.

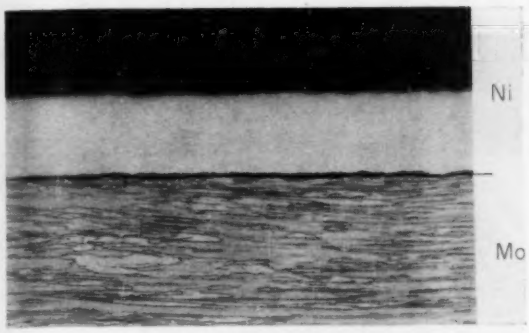


FIG. 5. Longitudinal section of 80-mil Mo rod electroplated with Ni that blistered when heated in air to 900°C. 10× before reduction for publication.

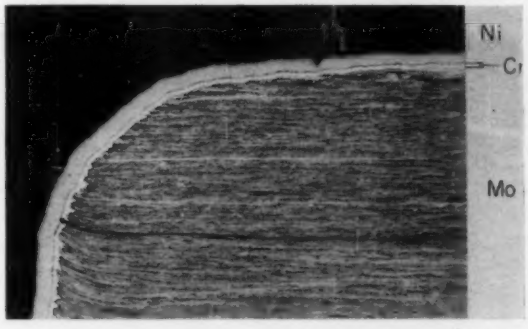


FIG. 6. Cr and Ni on laminated Mo sheet. 100× before reduction for publication.

Fig. 4A shows the Ni plate to be nonporous and to be apparently well bonded. Some porosity of the metal is apparent in a heated zone, however, as is shown in section B. A layer of NiO also is apparent in this section. Although NiO is very refractory (mp 1950°C), this oxide layer may not afford much protection to the underlying metal when it is thermally cycled because of the formation of cracks.

In section C, a zone very near that of section B, some alloying of Ni and Mo is apparent. This alloy formed only in islands, however, rather than in a continuous layer as did alloy between Cr and Mo. The formation of islands rather than a continuous layer of Mo-Ni alloy probably indicates imperfect bonding between the Mo and the electrodeposited Ni.

Section D shows a zone approximately at the maximum temperature, i.e., about 900°C. Islands of Ni-Mo alloy are connected in this zone, and this layer may well have afforded protection against oxidation in this zone.

While the Ni plating did not last as long at 900°C as a similar thickness of Cr, Ni might be serviceable as a protective coating. As was stated earlier, however, it was more difficult to obtain good adhesion of Ni than of Cr, and this characteristic of Ni probably contributed to blistering in Ni coatings.

Fig. 5 shows Ni plating on a specimen of 80-mil Mo rod, which blistered severely when heated to 900°C. A section of this plate in an unheated zone, as shown in Fig. 5, shows that it was not bonded to the base metal.

Because electroplated Cr cracked while Ni did not, it was thought desirable to cover the Cr plate with a layer of Ni. Two different types of multilayer coatings were examined, one a double-layer coating consisting of Cr and Ni, and the other a triple-layer coating consisting of Cr, Ni, and Cr. Double-layer coatings were attempted both with Cr as the initial layer and with Ni as the initial layer. Both types of coatings were successfully applied to 80-mil rods, but on flat specimens, attempts to plate Cr over Ni invariably caused the underlying Ni coating to peel from the Mo.

Of these various types of multilayer coatings, the double-layer coating in which Cr was the initial layer appeared to be the most promising.

Two outstanding features of this type of coating were: (*A*) If the layer of Cr was not too thick, the covering of Ni appeared to prevent the formation of cracks in the Cr layer. (*B*) The throwing power of Ni was better than that of Cr, and it usually covered faults or laminations in the Mo that extended through the Cr plate.

These properties of double-layer coatings of Cr and Ni are illustrated in Fig. 6 and 7 which are sections inside the heated zone of a flat test specimen.

However, blisters frequently formed inside the heated zone and often were centers of failure. Separation of metal to form a blister apparently occurred between the Ni and Cr layer, as is shown in Fig. 8. Laminations in the Mo, however, also may permit the formation of blisters, as is indicated in Fig. 9.

The tendency of Ni to buckle probably results because

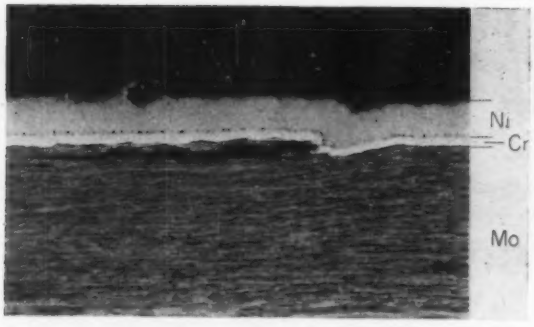


FIG. 7. Cr and Ni on laminated Mo sheet. 250× before reduction for publication.

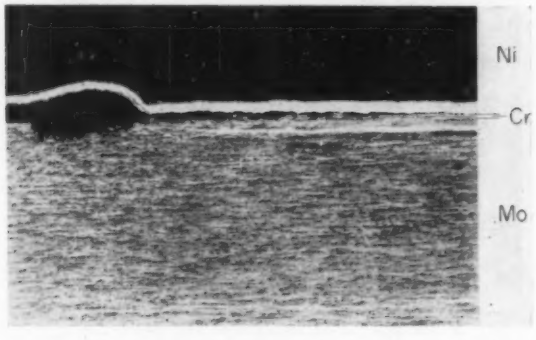


FIG. 8. Cr and Ni on Mo sheet in a zone that blistered when heated. 100× before reduction for publication.

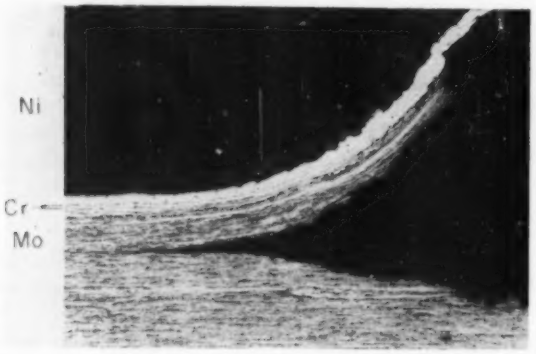


FIG. 9. Cr and Ni on Mo sheet in a zone that blistered when heated. 100× before reduction for publication.

of its high thermal expansion. This explanation is supported by the separation of coating on the edges of flat specimens, as is shown in Fig. 10. In this figure, as in Fig. 8, it appears that separation occurred between the Ni and Cr layers.

An objection to the triple-layer plate consisting of Cr-Ni-Cr is the tendency of the outer layer of Cr to crack. In some cases, this crack extended through the underlying layers of Ni and Cr. Fig. 11 shows such a crack in a coating as plated. Fig. 12 shows the same type of coating with cracks only in the outer layer of Cr. This

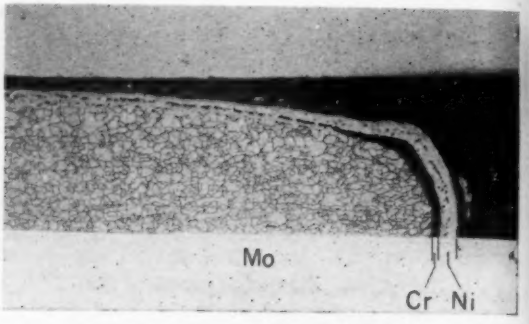


FIG. 10. Cr and Ni on edge of Mo sheet after 185 hr in air at 900°C. 100× before reduction for publication.

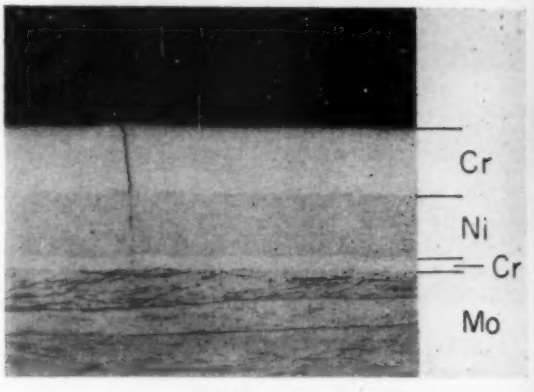


FIG. 11. Cr-Ni-Cr on Mo sheet. 250× before reduction for publication.

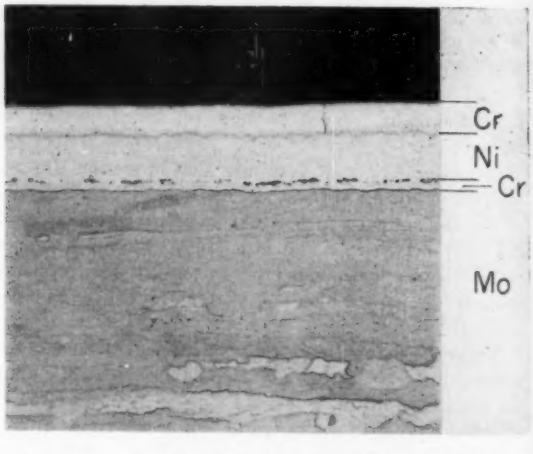


FIG. 12. Cr-Ni-Cr on Mo sheet after ½ hr in H at 1100°C. 250× before reduction for publication.

latter specimen was heated in H for the purpose of diffusing Cr into the Mo.

All of the multilayer coatings were effective in protecting Mo. Fig. 13 shows the structure of a double-layer coating of Ni over Cr on an 80-mil rod of Mo after 1000 hr at 900°C. It may be noted that the outer layer of NiO

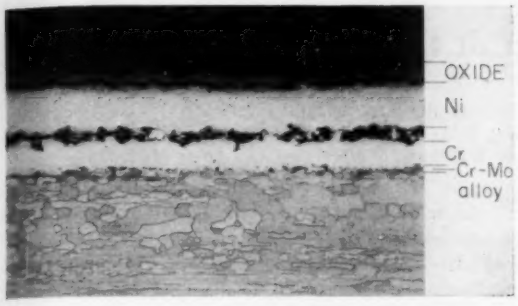


FIG. 13. Cr and Ni on 80-mil Mo rod after 1000 hr in air at 900°C. 250× before reduction for publication.

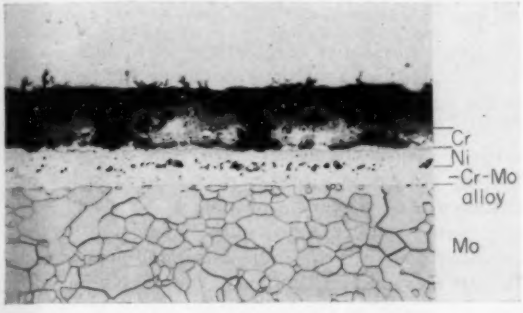


FIG. 14. Cr-Ni-Cr on Mo sheet after 185 hr in air at 900°C. 250× before reduction for publication.

is not cracked to the same extent as it was on samples of Mo coated with Ni only. Diffusion of Cr through the layer of Ni might have occurred to a sufficient extent to cause modification of the oxide layer on this specimen.

Fig. 14 shows a triple-layer coating of Cr-Ni-Cr on a flat specimen of Mo after 185 hr at 900°C. The outer layer of Cr does not appear to have afforded much protection to the underlying metal.

## CONCLUSIONS

Electroplated coatings of either Cr or Ni afford considerable protection to Mo at high temperatures, but both types of coatings have shortcomings and, if used singly, are not likely to produce consistent results.

From this study, it appeared that the principal problems with electroplated Cr were its tendency to crack and its relatively poor throwing power during plating. Cr forms a good bond with Mo, however, and the interfacial alloy between these two metals appears to have good oxidation resistance and probably has good ductility. Electroplated Cr may be superior to Ni for protecting Mo. Of different types of Cr plate, low-contraction Cr probably is superior to hard Cr. Electroplated Ni, in contrast, apparently did not form cracks and it effectively bridged flaws in the base metal, but the problem of obtaining good adhesion of Ni appeared to be more formidable than that for Cr.

Undesirable features of electroplated Cr, that is cracking and poor coverage, may be overcome to some extent by covering it with a layer of Ni. The Ni layer appears to be capable of covering many of the faults that extend through the Cr plate and also preventing the Cr from cracking when heated. Ni has high thermal expansion, however, and, therefore, must be well bonded or it may buckle and form blisters when heated.

Electroplated Cr over Ni is not desirable because of the formation of cracks that not only may cause rapid deterioration of the Cr but also may extend through the Ni layer.

## ACKNOWLEDGMENTS

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1957 JOURNAL.

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# Electrodeposition of Uranium at the Microgram Level

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ABSTRACT

The recovery of microgram and submicrogram quantities of U by electroplating has been studied, using radioactive U-233 as a tracer with and without the presence of microgram quantities of natural U as carrier. Optimum results were obtained in an ammonium oxalate medium with electrolysis at 80°–85°C being performed first in acidic solution and then in alkaline solution. A small Pt disk which fitted into a flow counter was used as cathode, and a Pt spiral served as anode. With 20 μg of U carrier present and a volume of 25 ml, an average recovery, based on alpha counting, of 94 ± 3% was obtained for amounts of U-233 ranging from 0.03 to 0.13 μg.

Several methods have been described for the analytical electrodeposition of milligram quantities of U (1–6). In acetate medium, up to 4 mg U were deposited (2); results were not accurate due to variation in composition of the plates. Use of an oxalate medium at 80°–85°C gave satisfactory results with about 3 mg U (2). Up to 0.5 mg U was plated quantitatively from fluoride medium at room temperature (3–5). Micro quantities of U were deposited from oxalate medium containing potassium hydrogen phthalate buffer by electrolyzing at 80°–85°C in two stages: first on the acid side, then on the alkaline side (6). In all these cases a Pt disk was used as cathode, and the plated films were ignited to $U_3O_8$.

The use of an Al-Zn disk as cathode in oxalate medium at *p*H 8.0–8.5 and 80°–85°C has been reported (7). Two German patents (8) describe the deposition of metallic U onto Pt and other surfaces from an organic solvent like acetone which exerts no oxidizing action.

Recovery of microgram quantities of U from human urine by electroplating for the determination of alpha activity has been examined (9). One microgram of enriched $U_3O_8$ (130 $\alpha$ counts/min/μg) was added to 100-ml urine samples. After evaporation to dryness and ignition to destroy organic matter, the residues were dissolved; Ca was removed by double precipitation as the oxalate; and U was then electroplated at 80°C onto a Ni disk from the resulting ammonium oxalate medium of *p*H 9.6, using a current of 3 amp for 60 min. The recovery of U from 18 samples was 85 ± 4% with a precision of ±16% on a single sample.

Previous studies on the electrodeposition of U such as those cited above have generally been applicable only to the recovery of milligram amounts of U. Attempts to plate microgram quantities of U, usually present in rather small volumes of solution, resulted in U recoveries which were both low and variable. Apparently no reliable results have been reported for electrodeposition of submicrogram amounts of U. Consequently, the present study was initiated in an attempt to define conditions for more nearly quantitative recovery by electrodeposition of microgram amounts of U. In addition, an attempt was made to investigate the feasibility of electrodeposition of submicrogram amounts of U and to define the reproducibility of the procedure for microgram levels of U.

Initially, qualitative observations were made on the plates obtained from solutions containing $10^{-10}$ g U; such studies were deemed more significant than quantitative orientative work using much larger quantities and titrimetric or colorimetric measurement, since it was not felt that any proof of quantitative deposition at higher concentration, e.g., milligram amounts of U, would necessarily permit valid prediction of the behavior at very low concentrations. Moreover, the nature and appearance of the plate for milligram amounts of U could not be judged with any degree of reliability with respect to its suitability for radiochemical counting.

Quantitative studies were then made at microgram levels of U using a tracer technique and counting. The procedure finally developed may be applied for the recovery of $10^{-7}$ or $10^{-8}$ g of radioactive U, using $10^{-5}$ g of carrier natural U. At the milligram level, self-absorption phenomena become an important factor in counting. The present method uses for electrodeposition an ammonium oxalate medium, which has been found to be superior to citrate, tartrate, and phthalate media, inasmuch as the latter media introduce some difficulty in *p*H control during electrolysis.

The present procedure of recovering U by electrodeposition, and of measuring it by counting the activity of the plate, has been applied as the final separation stage and the measuring step in an analytical procedure for the determination of submicrogram quantities of U when present in admixture with large amounts of fission products (10).

## EXPERIMENTAL

*Apparatus.*—The electroplating assembly consisted of a d-c power supply (Fisher Scientific Co. Powerhouse); a Tracer-Lab E-16 electrolysis cell containing a spiral Pt wire anode [a 10-in. (25 cm) length of 1-mm diameter wire, about 3 in. (7.5 cm) of which were wound into a flat spiral of 0.5-in. (1.25 cm) OD], a Pt disk cathode, and a motor-activated 500 rpm glass stirrer; and a simple external water bath for controlling the temperature of the electrolysis cell.

The cathode was a Pt disk or planchet, 0.15 mm thick by 25 mm diameter, obtained from the American Platinum Works. New Pt disks were pretreated by a hot $HNO_3$

wash, a water wash, then flaming; they were stored in a cell under water until used. For some of the runs, used Pt disks containing a $U_3O_8$ film were cleaned by repeated hot concentrated $HNO_3$ treatment and flaming. When their activity was close to the background level, the disks were considered good enough for use in another plating process. These disks were counted as blanks before plating and were stored under water until used.

A Model 952 windowless flow counter (2″ cathode) and a Model 1070 scaler (both made by the Atomic Instrument Company, Cambridge, Mass.) were used to count the alpha emission of the plated disks. The counting gas employed was Q-gas (99.05% He and 0.95% isobutane), which was dried with indicating Drierite (8-mesh), followed by Dehydrite.

*Materials.*—All chemicals used were of reagent grade.

The radioactive U-233 was obtained as a nitrate solution from the Oak Ridge National Laboratory; isotopic analysis gave 1.0–1.5% U-232 and 98.5–99% U-233 ($\alpha$ 4.82 mev; $t_{\frac{1}{2}} = 1.68 \times 10^5$ *y*). The original solution (13 μg U-233) was diluted to 100 ml which was about 0.01*N* in $HNO_3$; aliquots of the latter solution containing $1.3 \times 10^{-3}$ g U/ml were taken for the experimental work. The activity per microgram of U-233 was determined, as subsequently described, to be 7700 ± 88 counts/min (background subtracted).

The carrier U was prepared from natural uranium nitrate (Baker and Adamson). The stock solution contained about 1 mg U/ml (0.01*N* in $HNO_3$), from which, after proper dilution, the solution used to furnish carrier, which contained about 10 μg U/ml (0.01*N* in $HNO_3$), was prepared.

## Qualitative Studies on the Electrodeposition of Uranium

Three procedures were investigated to see what happened on electroplating about $10^{-10}$ g of U. In procedure A, based on that of Manning, Cali, and Phillips (6), the electrolysis cell solution was prepared by diluting 1 ml uranium nitrate solution ($10^{-10}$ g U) to 25 ml and adding 5 ml saturated ammonium oxalate solution, 10 ml buffer solution (5.85 ml 0.217M potassium hydrogen phthalate and 4.20 ml 0.298M NaOH), and 2 drops methyl red indicator; the *p*H was 6.48. Electrolysis was carried out for 45 min at 80°–85°C, using an applied potential of 9 v with a resulting current flow of about 0.2 amp; the stirrer speed was about 500 rpm. Then, 1 drop (0.01%) phenolphthalein was added, followed by sufficient 6M $NH_3$ to turn the solution pink; the plating was continued for 10 min more with additional indicator and $NH_3$ being added as needed to keep the solution pink; temperature, current, etc., were the same as before.

In procedure B, 1 ml uranium nitrate solution ($10^{-10}$ g U), 17.35 ml 0.1003M citric acid solution, 1 ml of 6M $NH_3$ solution, and 4 drops phenol red indicator (yellow at *p*H 6.50) solution were diluted to 25 ml. Electrolysis was performed as before at *p*H 6.50 for 45 min. $NH_3$ was added until the solution was red; more $NH_3$ and indicator were added, as necessary, to keep the solution red as the deposition was continued for 10 min more.

Procedure C was the same as procedure B, except that 21.0 ml 0.0927M tartaric acid solution was substituted for the citric acid and 0.75 ml 6M $NH_3$ was added.

At the end of electrolysis the current was left on as the spent electrolyte was siphoned off, and the cell and its contents were washed repeatedly with distilled water until the solution remaining in the cell was colorless. The circuit was then disconnected and the cell disassembled. The Pt cathode was rinsed with water followed by acetone, air dried, then ignited for about 10 min to $U_3O_8$.

The plates obtained by the three procedures were smooth, shiny, and adherent, showing bright interference colors. Procedures B and C seemed to be much simpler than A, at the same time giving deposits of better appearance. An additional advantage in the use of citrate or tartrate medium was that gas evolution at the electrode was much less than that in oxalate. Unfortunately, later quantitative studies showed that the use of citrate, tartrate, and phthalate introduced certain difficulties in the procedure; the latter were apparently due to reactions of these organic compounds which gave rise to very dark brown solutions. Consequently, an oxalate medium was used generally similar to that of procedure A except for the omission of phthalate.

*Use of* Al-Zn *disks.*—Attempts to use as cathode an Al disk coated with Zn were unsuccessful. In no case was the coating of Zn on Al smooth; as a result, electrodeposition was not at all satisfactory. An added disadvantage in actual use would be chemical contamination of the U sample when its recovery was desired. While Al-Zn disks are less expensive than Pt disks, the latter do permit recovery of uncontaminated U. The same considerations would be against the use of Ni or other disks.

*Electrodeposition from organic solvents.*—In an attempt to explore possibilities of plating U from organic solvents, the electrical resistances of various organic mixtures were examined in the electrodeposition apparatus described; results are summarized in Table I. Attention was focused on such compositions as could be achieved readily subsequent to a cupferron extraction of U(IV) which would be

TABLE I. *Qualitative studies of the conductivity of solution containing acetone, ethanol, and ethyl ether*

| Run No. | Solution composition | Voltage applied, v | Current flow, ma |
|---|---|---|---|
| 1 | 20 ml acetone (containing 0.8 g LiCl) + 10 ml ether | 9 | 0.0 |
| 2 | 20 ml acetone (0.8 g LiCl) + 2 ml ether | 9 | 0.6 |
| 3 | 25 ml ether (1.0 g LiCl) + 5 ml alcohol | 9 | 0.0 |
| 4 | 5 ml ether (0.2 g LiCl) + 20 ml alcohol | 9 | 1.5–2.0 |
| 5 | 10 ml ether + 10 ml alcohol (0.25 g LiCl) + 0.2 ml water | 6 | 3.0 |
| 6 | 10 ml ether + 10 ml alcohol (0.25 g LiCl) + 0.5 ml water | 6 | 3.1 |
| 7 | 10 ml ether + 10 ml alcohol (0.2 g LiCl) + 1.0 ml water | 6 | 3.3–3.5 |
| 8 | 12 ml ether + 8 ml alcohol (0.2 g LiCl) + 0.5 ml water | 6 | 2.2 |
| 9 | 15 ml ether + 5 ml alcohol (0.12 g LiCl) + 0.5 ml water | 9 | 0.5 |

an efficient way of separating U from many other elements. The alcohol used in Nos. 3–9 was 95% ethanol. Although media of moderately good conductance were found, no electrodeposition of U from solutions of uranium(IV/III) cupferrate in such media was realized.

### Quantitative Studies on Electrodeposition of Uranium at Microgram Level

*Plating procedure.*—The desired volume of U-233 solution was added to the electrolysis cell, followed by about 20 μg natural U carrier (uranyl nitrate solution), 5 ml saturated ammonium oxalate solution, 1 drop 6M HCl, 1 drop methyl red indicator, and 6M $NH_3$ until the solution was yellow. $HNO_3$ (6M) was then added until the indicator turned pink plus 2 or 3 drops in excess. The volume was about 20 ml. The cell was placed in a water bath, maintained at 80°–85°C, and the anode rotated at about 500 rpm. The solution was electrolyzed for approximately 30–45 min, using an applied potential of about 9 v with a resulting current flow of approximately 0.8–1.0 amp; from time to time $HNO_3$ and indicator were added dropwise to keep the solution pink. Then, 1 drop of phenolphthalain (0.01%) (more, as needed) and 6M $NH_3$ (more, as needed) were added dropwise to turn the solution pink, and the plating continued for 60–75 min more; temperature, current, etc., were almost the same as before.

The washing procedure at the end of electrolysis was the same as that previously described; the Pt disk was rinsed with water, followed by acetone, and air dried. It was then ignited for 10 min to $U_3O_8$, cooled to room temperature, and counted in a windowless flow counter.

*Procedure for alpha counting.*—With the counter set in "count" position, an initial flushing was done for 5 min with the pressure regulator gauge reading about 2 lb/in.$^2$ and the gas flow being about 100 bubbles/min. Then the instrument was set in "load" position and the sample was introduced into the sample compartment. The counter was rotated to "flush" position, kept there for about 2 min, then moved to the "count" position. (The gas flow rate was then about 60 bubbles/min.)

The voltage plateau for alphas using pure U-233 was checked periodically. The operating voltage was 1550–1575 v, and discriminator setting was fixed at around 16–18. Betas are not counted under these conditions, as was noted by using a pure beta-emitting sample of Sr-90. Each U plate was counted over a sufficient period of time to give the desired statistical accuracy (±1–2% relative probable error). For calibration, a standard sample of $U_3O_8$ (National Bureau of Standards No. 836-5; 16.3 alpha counts/sec, assuming 50% geometry) was counted, then the unknown sample was counted. This was repeated five or six times and the average values were taken. Readings were fairly reproducible within statistical error. The background level of the instrument was 60–70 counts/min.

The calibrated activity of the plated sample was compared to the activity of the U-233 solution taken. The latter was determined by pipetting a 1-ml aliquot of the U-233 solution ($1.3 \times 10^{-8}$ g/ml) into a small 10-ml beaker by means of an ultramicro pipet, transferring the solution in portions by a medicine dropper with $HNO_3$ rinses onto a Pt planchet, evaporating under an infrared heater, igniting to $U_3O_8$, and counting the planchet. Five or six such samples were measured; the average activity was 7700 ± 88 counts/min/μg U-233.

*Electrodeposition of U.*—Results for the direct electroplating of U-233 in the presence of carrier are presented in Table II. The plates obtained were very smooth, shiny, and adherent, showing brilliant interference colors. If the first two runs are omitted because of their large error due largely to the low count, an average recovery of 94% ± 3% was obtained, after making correction for the activity of the 20 μg natural U used as carrier (15 ± 3 counts/min). Samples having 100–200 counts/minute (Nos. 1–4) were counted to give totals of 1000–2000 counts (relative probable error of ±2%), and those having 500 counts/min and higher activity were counted so as to give a total of 5000 counts (relative probable error of ±1%). Since only the percentage recovery of U-233 was required, disks containing evaporated and ignited aliquots of U-233 solution were used as a comparison for the plates obtained from electrodeposition.

*Influence of carrier on electrodeposition of U-233.*—Re-

TABLE II. *Electrodeposition of U-233 with 20 μg of natural U Carrier*

| Sample No. | U-233 taken, g | Counts/min and standard deviation | Recovery, % (corrected for carrier activity) |
|---|---|---|---|
| 1 | $1.3 \times 10^{-8}$ | 98 ± 9.9 | 82 |
| 2 | $1.3 \times 10^{-8}$ | 97 ± 9.9 | 81 |
| 3 | $2.6 \times 10^{-8}$ | 200 ± 14.1 | 91 |
| 4 | $2.6 \times 10^{-8}$ | 195 ± 14.0 | 89 |
| 5 | $6.5 \times 10^{-8}$ | 505 ± 22.5 | 97 |
| 6 | $6.5 \times 10^{-8}$ | 490 ± 22.1 | 94 |
| 7 | $13 \times 10^{-8}$ | 1004 ± 32.0 | 97 |
| 8 | $13 \times 10^{-8}$ | 1010 ± 32.0 | 98 |

Mean recovery (samples 3–8): 94.3%.
Standard deviation of the mean recovery: 3.0%.

TABLE III. *Effect of carrier on the recovery of U-233 by electroplating*

| U-233 taken | | Natural U carrier taken, μg | U-233 activity found, counts/min | Recovery, % (corrected for carrier activity) |
|---|---|---|---|---|
| Mass, g | Activity, counts/min | | | |
| $3 \times 10^{-8}$ | 324 ± 17 | 10 | 284 ± 17 | 85.4 |
| $13 \times 10^{-9}$ | 1200 ± 35 | 0 | 840 ± 29 | 70.0 |
| $13 \times 10^{-9}$ | 1200 ± 35 | 10 | 1140 ± 34 | 94.6 |

TABLE IV. *Effect of carrier concentration on recovery by electroplating of 0.065 μg of U-233*

| Natural U carrier taken, μg | U-233 recovery, % |
|---|---|
| 50 | 96 |
| 20 | 101 |
| 10 | 102 |
| 5 | 95 |
| 2 | 70 |
| 1 | 84 |
| 0 | 77 |

coveries of 0.01–0.1 μg U-233 with no carrier present averaged about 70% (63% for 0.013 μg, 77% for 0.065 μg, and 70% for 0.13 μg). A series of runs using various amounts of carrier indicated that the presence of about 10–20 μg natural U as carrier was requisite for a satisfactory recovery of submicrogram quantities of U-233 (Tables III and IV). The figures in the last columns of Tables II, III, and IV have been corrected for carrier activity by subtracting 0.75 counts/min/μg of carrier from the observed counts/min (11).

In Table IV, the lower (apparent) recovery with 50 μg of carrier than the recovery with 10 or 20 μg, is indicative of the fact that self-absorption becomes a factor at this level.

*Miscellaneous observations.*—Recoveries using minimal electrolysis times of 30 min in acidic solution plus 60 min in alkaline solutions at 9 v applied were sometimes low. A safer specification is to maintain a current of 1.0 amp for 60 min on the acidic side and 90 min on the basic side.

The form in which U electrodeposits at a cathode is not definitely known, but it is thought to plate as a hydrous oxide (12, 13). In any event, the plate after ignition in air has been shown to be $U_3O_8$.

Attention should be called to the fact that current and time requirements for microgram level electrodeposition bear no relation to theoretically predicted requirements based on reasonable current efficiencies. Some of the quantitative studies at the milligram level have specified 10–15 min electrolyses at reasonable voltages and amperages; however, conditions such as 1 or more amp at 9 v for 1–2 hr are requisite at the microgram level. While the reasons for such a large discrepancy are not at all obvious, it is true that some precedent exists in more familiar and reversible systems. For example, a given arrangement which deposits 99.5% of a 0.5 g sample of Cu in less than 1 hr may yet require another full hour to plate out the next 0.4–0.5% (14).

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# Influence of Impurities on the Photoconductance of Zinc Oxide

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ABSTRACT

The photoconductance of pure ZnO and ZnO with known impurities, both in powder form, has been measured using a condenser method. When irradiated by light, ZnO undergoes a "memory mechanism" which depends on the past irradiation history. It is suggested that the memory is caused by formation of traps independent of charge carrier formation. The concentration of traps is a function of impurity concentration and temperature. Consistent results in agreement with those of previous investigators could be obtained, but it is shown that this depends on predetermining the irradiation history of the samples.

The rate of excitation is given by $d\sigma/dt = kI^n$ where both $k$ and $n$ are sensitive to impurity concentration and temperature. The decay of photoconductance is largely the sum of two first order processes, but there can be no assignment of time constants to either hole or electron decay. A qualitative kinetic mechanism is proposed which agrees with phenomena observed in this investigation.

The photochemical formation of $H_2O_2$ as catalyzed by solid ZnO has received considerable attention recently (1–3). It has been shown in this laboratory that impurities in the ZnO affect this reaction rate (4). A fuller knowledge of the role of ZnO requires examining some of the details of the processes that follow light excitation; for this reason it was decided to study the photoconductance of ZnO. The relation of semiconductivity to catalysis has been pointed out (5–7), and the catalysis of nonphotochemical reactions on ZnO has been studied from this standpoint (8–10).

Previous workers have used very different samples of ZnO and, as a consequence, their results have not been comparable. Mollwo and co-workers (11–13) and Weiss (14) used thin films (0.1–0.3 $\mu$) made by oxidizing Zn metal films evaporated onto quartz. They first presented the following equations as characteristic of photoeffects in ZnO:

$$i_L = ki_0^{2/3}I^{1/2} \qquad \text{(I)}$$

$$(di/dt)_1 = k_1 i_0 I \qquad \text{(II)}$$

$$(di/dt)_2 = k_2 i_L^2 i_0^{-2/3} \qquad \text{(III)}$$

where $i_L$ is the saturation or equilibrium photocurrent, $i_0$ is the dark current, $I$ is the light intensity, $(di/dt)_1$ is the slope of the initial rise of the photoconductivity with time, and $(di/dt)_2$ is the slope of the initial decay of photoconductivity. It is shown later that Eqs. (I) and (II) are true only under special conditions and that under other conditions, exponents of $I$ depart from the above values. Warschauer (15) and Melnick (16) used sintered pellets of ZnO.

In the present research photoconductance was studied on ZnO samples drawn from large prepared batches which also furnished samples for several catalytic chemical studies in this laboratory. The catalytic experiments required this material to be in powder form. The experimental method best suited for the investigation of photoconductivity of powders is the condenser method (17–19) in which the powder is put between the plates of a condenser. One plate of the condenser is transparent so that the sample can be irradiated, and the subsequent changes in the dielectric are measured.

## EXPERIMENTAL

*Preparation of the* ZnO *powders.*—ZnO samples were prepared by starting with a $ZnSO_4$ solution[3] which had been especially purified for phosphor preparation. The solution was further treated, and Zn was precipitated as the oxalate with twice-recrystallized oxalic acid. The purified $ZnC_2O_4$ was decomposed to ZnO by firing in air at 410°C to constant weight. The sample without intentionally introduced impurities is called "pure" ZnO.

Impurities were introduced by adding to $ZnC_2O_4$ a soluble decomposable salt of the desired substance. The resulting slurry was evaporated to dryness with stirring, then fired at 410°C for 4–6 hr. Impurities were Li, Cu, Al, and Ga. The amounts were calculated to replace 0.01%, 0.1%, and 0.5% of the Zn atoms by impurity metal atoms. In the case of the Li samples it was necessary after the initial 410° firing to heat the ZnO to 600° to obtain constant weight. These samples were then cooled and held at 410° for 4 hr. [The ZnO samples containing Ga, for example, are referred to as "gallium samples" or as "ZnO-Ga (0.01%)"].

Analysis showed that the samples contained on the average about 99% of the expected Zn content for ZnO. Spectroscopic and other analysis showed the laboratory samples to be of very high purity. X-ray analysis gave the expected pattern for ZnO. Surface areas were measured (10) by a modified BET method and the samples were found to fall in the range of 10–20 $m^2/g$.

Since it has been shown (8) that foreign oxides affect the

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[3] Obtained from the Chemical Division of the General Electric Co., Cleveland, Ohio.

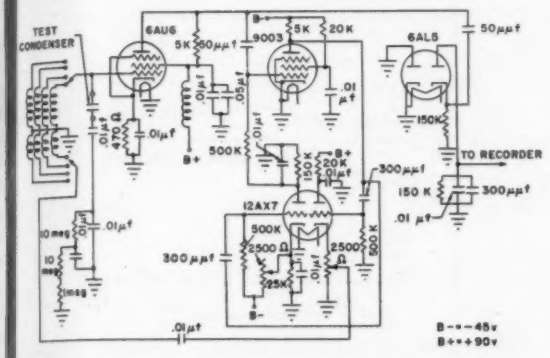



FIG. 1. Circuit for the measurement of the change in $Q$ of the experimental condenser.

conductivity of ZnO, and presumably this is possible only when solid solutions are formed, it was assumed that the added impurities went into solid solution, as supported by the dark conductivity of the samples.

*Apparatus.*—In previous work with the condenser method the change in capacitance was usually measured. Because a change in $Q$ [$Q$ = ($X_L/R$) = Inductive reactance/resistance] rather than a change in capacitance is more indicative of liberated photoelectrons, the measuring circuit in this research was designed with this point in mind. The oscillator always maintained itself on the resonance peak and was driven via the feedback coil with a constant driving voltage (Fig. 1). The RF signal was filtered, rectified, and recorded as millivolt changes on a Speedomax recorder which had a 1-sec full range sweep time. The circuit was calibrated by putting noninductive resistors of suitable value across the condenser, which had plain paraffin as dielectric. The resistors simulated the loss the condenser undergoes during irradiation. A calibration curve was made by plotting the change in millivolts appearing on the recorder against $\sigma$ where $\sigma = 1/\text{resistance}$. Thus $\sigma$ is proportional to the number of charge carriers released during irradiation and is called here the "photocurrent," or more properly the "photoconductance."

Fig. 2 shows the construction of the experimental condenser. It was machined from brass with Bakelite for insulation. The transparent electrode was electrical conducting glass.[4] A separation of 50$\mu$ was maintained between the plates of condenser. For measurements at low temperatures, the condenser was placed in a toluene thermostat.

The light source was a Hanovia Mercury Arc Sc5043. The various wave lengths were isolated with a Bausch and Lomb Grating Monochromator Type 33-86-40. The light intensity was measured with an Eppley Copper Constantan Spectrum Type Thermopile.

*Procedure.*—The powder was prepared for use as dielectric in the following manner: 6 g of paraffin was placed in a 20 x 70 mm vial and melted in a boiling water bath and 1.5 g ZnO was thoroughly mixed in. The mass was centrifuged to give a high density of ZnO in paraffin. It did not produce any undesired preferential packing of sample since slices from the top or bottom of the pellet gave the same results. The resulting pellet was allowed to cool and then was cut with a microtome into slices 50$\mu$ thick. The slices were kept in the dark until they were irradiated for measurement.

For measurement, a slice was placed in the condenser and the assembly completed. The condenser was placed in the thermostat and irradiated with the desired wave length. The resulting change in $Q$ was recorded as a change in millivolts vs. time on the recorder.

[4] Obtained from the Corning Glass Works, Corning, N. Y.

### *Experimental Results*

In general, each sample was characterized by a dark conductivity $\sigma_D$ which appeared as a steady reading on the recorder. The dark conductivity was estimated by comparing the loss of the condenser using ZnO-paraffin as dielectric with the loss when the dielectric was plain paraffin. Ideally each grain is isolated from every other grain and the photoliberated electron is confined to the grain in which it originates.

When the light impinges on the sample there is a rapid increase in the number of charge carriers and this appears as a sudden change in millivolts on the recorder. After a time, a new equilibrium value of $\sigma$ is reached. In many cases $\sigma$ goes through a pronounced maximum and finally settles down to a new lower equilibrium or saturation value, $\sigma_S$. When the light is shut off, the photocurrent decays toward the value $\sigma_D$. Fig. 3 gives a typical curve. The value of the maximum photocurrent is $\sigma_M$; the saturation or equilibrium photocurrent is $\sigma_S$. The eventual value of the current after the light is shut off and rate of decay becomes essentially zero is $(\sigma_D)_\infty$. This value is taken as the end of the observable decay.

Preliminary experiments were made to check the applicability of equations (I), (II), and (III) to the samples and methods of this research. These were carried out on Merck Reagent ZnO Lot No. 53551. It eventually became apparent that the ZnO was undergoing a "memory mechanism" during irradiation in that when the light was shut off and the photocurrent decayed to $\sigma_D$, the samples were not the same as before irradiation. If the same experiment was repeated immediately neither $\sigma_M$ nor $\sigma_S$ was as large as in the first experiment. Weiss (14) was able to

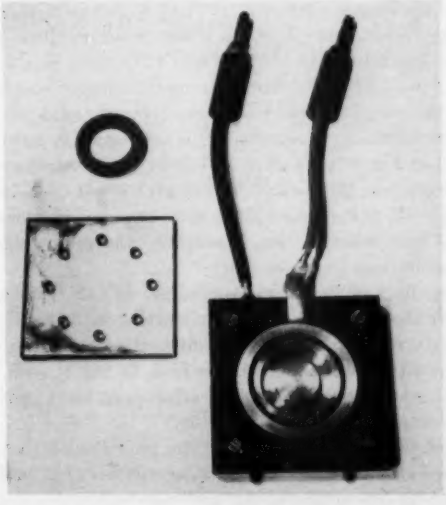


FIG. 2. Experimental condenser

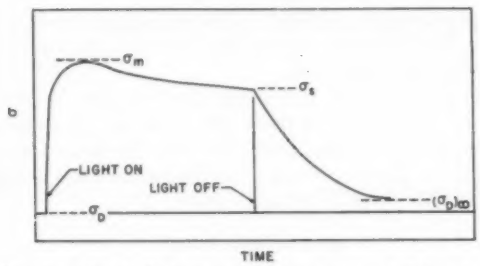



FIG. 3. A typical photoconductance curve defining terms used.

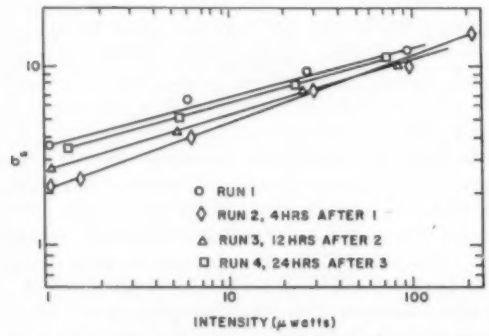



FIG. 4. Effect of various experimental time sequences, illustrating the memory effect (Merck Reagent ZnO).

reproduce equations (I), (II), and (III) only by doing his experiments in a prescribed fashion. Before each measurement he pre-irradiated his samples with light of $\lambda = 280$ m$\mu$ and then exposed them to the desired wave length.

In the present work a wide variation in the value for the exponent of $I$ in eq. (I) was obtained depending on how the experiment was carried out. Fig. 4 shows how the exponent depends on the previous irradiation history. In Fig. 4 the exponent is given by the value of the slope of the plot of log $\sigma$ vs. log $I$. The first point taken on each curve was the lowest intensity point; the sample was allowed to decay apparently fully and the next higher intensity point was taken immediately. Each point was taken in this manner until the curve was completed. From Fig. 4 the stages of recovery of the sample can be followed by the various time intervals between curves. Run 2 was taken 4 hr after Run 1, Run 3 was 12 hr after Run 2, and Run 4 was 24 hr after Run 3. If another sample was taken and the same sequence of measurements made, reproducible results were obtained. It is interesting to note that Run 1 in Fig. 4 has a slope of 0.32 in apparent agreement with equation (I). Values of about 0.3 could be obtained at will with new samples if the same sequence of measurements was followed, i.e., essentially the pre-irradiation treatment used by Weiss (14).

The effect of variation in sequence of measurement is further shown in Fig. 5. A curve starting with the highest intensity point taken first is compared with a curve with the lowest intensity point taken first. It can be seen that the curves do not coincide, indicating again the sensitivity of the sample to irradiation history.

Since oxygen plays a role in the photoconductivity of sintered zinc oxide samples (16), it was felt that perhaps oxygen on the surface of the ZnO was responsible for the memory by contributing a slow step to the rate processes.

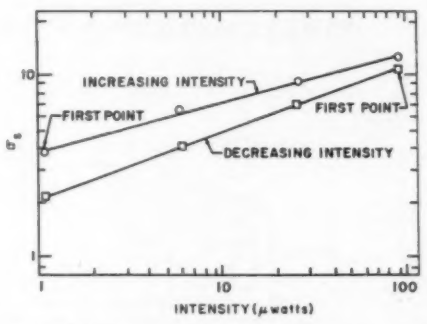



FIG. 5. Effect of irradiation history on memory (Merck Reagent ZnO).

Therefore, an experiment was carried out eliminating oxygen by mixing ZnO into paraffin under vacuum. The powdered ZnO was outgassed for several hours at 235°C, then mixed under vacuum with melted paraffin, which had also been outgassed. All subsequent steps were carried out in an oxygen-free N atmosphere. The sample had a much greater memory effect in that $\sigma_M$ and $\sigma_S$ were much less on the repeat measurement than on the first. It was also noted that the photoconductance curve for the oxygen-free sample exhibited a more prominent maximum. Thus it was apparent that the memory could not be removed by removing oxygen from the surface of the ZnO. These results cannot be correlated exactly with the effect of oxygen on the surface because on outgassing the ZnO became slightly colored, and this darkening has been interpreted as indicating interstitial reduced zinc (12, 22, 23). Samples used in this research were equilibrated with air and paraffin at the temperature of the boiling water bath.

Fig. 4 shows that the sample had substantially recovered after 12–24 hr, so it was decided to wait 24 hr between measurements to insure recovery, as in Fig. 6. The plot is no longer a straight line but shows curvature in contrast with the curves in Fig. 4.

The general procedure established in the preliminary experiments with the Merck sample was then applied to the other samples containing impurities. Fig. 7 shows a number of characteristic photoconductance curves for these samples. The figures are arranged in rows according to impurity type and in columns according to the experimental conditions of wavelength and temperature. All the samples are characterized by a saturation photocurrent, and many show pronounced maxima at room temperature. At 367 m$\mu$ all curves show at least a slight

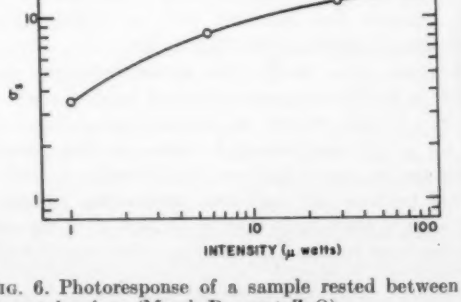



FIG. 6. Photoresponse of a sample rested between experimental points (Merck Reagent ZnO).

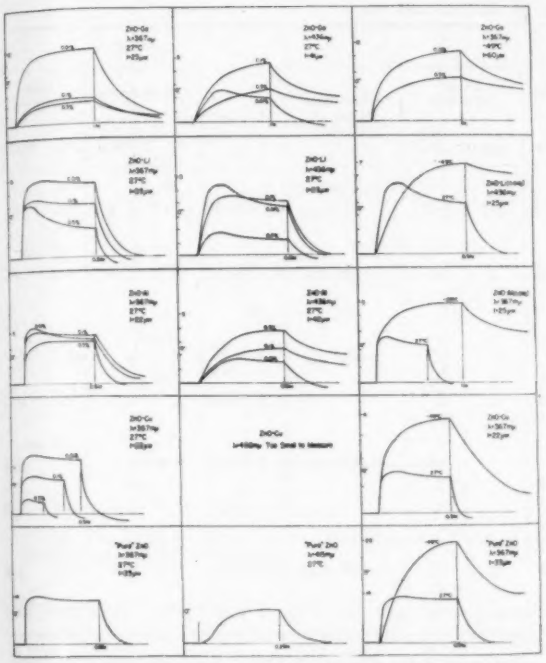


FIG. 7. Summary of a number of photoconductance vs. time curves, showing the build-up and decay. The subfigure in the third column and fourth row (Fig. 7—III—4) should be labelled ZnO-Cu (0.01%).

maximum except the samples containing Ga. In all cases but one to be discussed later, the photocurrent decreased when the light was shut off, but the current did not necessarily decay to the original dark current before illumination. The current, $(\sigma_D)_\infty$, may be either larger or smaller than $\sigma_D$, although in many cases it became equal to $\sigma_D$.

A number of measurements were made at −49°C also. The effect of temperature can be seen by comparing the curves in the third column of Fig. 7 with other appropriate curves. The saturation photocurrents are greater at −49°C than at room temperature for every case studied except Ga samples at 436 mμ. All of the maxima obtained at room temperature disappear at the lower temperature. The rise and decay are much slower, and the decay is very incomplete in all cases.

The effect of light intensity is shown for Ga in Fig. 8. All samples gave similar results in that the current values increased regularly at low intensities and decreased at very high intensities. The fact that the curve bends down at the higher intensities is taken to mean that even any one measurement is subject to error because of slow reversible changes in the sample due to illumination, i.e., the sample acquires an irradiation history even during the course of one measurement, and this memory effect is more pronounced at higher intensities.

If the values for the initial slope, $(di/dt)_1$, are plotted against light intensity on a log-log scale, good straight lines are obtained for several hundred-fold variation in intensity (Fig. 9). Thus the data can be fitted to an equation of the form $(di/dt)_1 = kI^n$. The value of the exponent, $n$, as determined from the slopes of the log-log plot, was found to be about 1 for all samples at room temperature at 367 mμ. However, at the lower temperature and at other wave lengths, the values of the exponent depart quite widely from unity. The fact that $n$ can be different from 1 is indicative of a complicated process. Values of $k$ and $n$ are listed in Tables I and II. At very low light intensities, all samples showed a slight but definite induction period before the onset of photoconductance. The period varied from ¼ to 1½ sec. No induction was observed at lower temperatures and longer wave lengths, presumably because higher intensities were required to yield measurable photoconductance.

The decay curves could be analyzed as consisting of two first-order rate processes. Over 98% of the decay could be fitted to two first-order processes by proper choice of the asymptote for $(\sigma_D)_\infty$. The adjustment for the asymptote was no more than 1–2% of the decay. Applicability of the method is illustrated in Fig. 10 showing a typical plot of a sample containing Al impurity. The shorter time constants were of the order of ¼–2 min and the longer, about 4–20 min. Specific values are also given in Tables I and II. (It should be recalled here that there are other still slower decay processes which are responsible

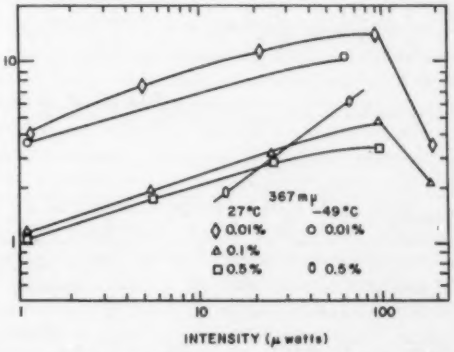



FIG. 8. Photoresponse of various ZnO-Ga samples as a function of light intensity and at two temperatures.

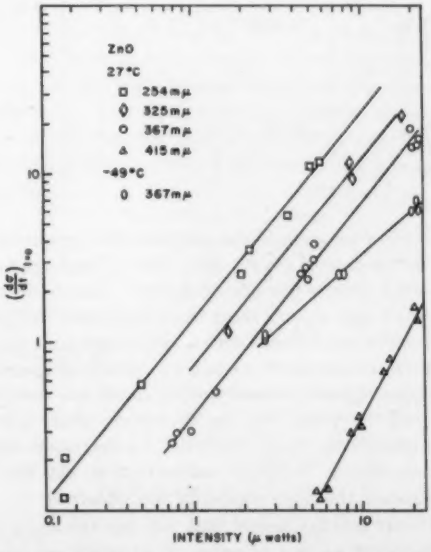



FIG. 9. Typical set of curves showing the effect of light intensity on the initial slopes of photoconductance. These plots are used to evaluate $k$ and $n$ in $d\sigma/dt = kI^n$.

TABLE I. *Summary of data at 367 mμ*

| Sample | 27°C | | | | | | | | | | −49°C | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $k$ | $n$ | Dark current | Low intensity | Medium intensity | High intensity | Decay constants | | Max. wave length of response | | $k$ | $n$ | Low intensity | High intensity |
| | | | $\sigma_D$ | $\sigma_S$ $(\sigma_D)_\infty$ | $\sigma_S$ $(\sigma_D)_\infty$ | $\sigma_S$ $(\sigma_D)_\infty$ | $t_{1/2}$ min | $t_{1/2}$ min | | | | | $\sigma_S$ $(\sigma_D)_\infty$ | $\sigma_S$ $(\sigma_D)_\infty$ |
| ZnO | | | | 1 μw/cm² | 25 μw | 90 μw | | | cut off at | | | | 1 μw | 67 μw |
| | 0.36 | 1.23 | 2.5 | 0.6 0.0 | 6.5 0.0 | 12.5 0.0 | ¼–½ | ½–3 | 425 mμ | | 0.14 | 0.87 | 2.4 1.6 | 28 18 |
| Cu | | | | | 22 μw | 80 μw | | | | | | | 3 μw | 63 μw |
| 0.01% | 0.32 | 1.1 | 5 | | 1.2 −0.1 | 1.8 −0.2 | ¼ | 2 | ~436 mμ | | 0.40 | 0.91 | 2.8 0.8 | 4.5 0.7 |
| 0.1 | 0.05 | 1.1 | 4.2 | | | | | | | | | | | |
| Li | | | | 1 μw | 24 μw | 72 μw | | | | | | | 1 μw | 65 μw |
| 0.01% | 2.2 | 1.0 | 6 | 2.4 0.0 | 5.2 0 | 12 0 | ½ | 2¾ | ~600 mμ | | 1.3 | 0.7 | 8 8 | 40 39 |
| 0.1 | 1.0 | 1.0 | 7 | | 2.8 −0.1 | 4 −0.1 | ¾ | 3¼ | | | | | 3.8 μw | |
| 0.5 | 1.4 | 1.16 | 5 | 0.8 0.0 | 1.5 −0.4 | 2.5 −0.5 | ¼ | 5 | | | 1.5 | 0.75 | 4 1.3 | 9.5 4.7 |
| Ga | | | | 1 μw | 25 μw | 90 μw | | | | | | | 1 μw | 60 μw |
| 0.01% | 1.4 | 1.17 | 4 | 3.8 0.4 | 12 0.8 | 15 0 | | 8½ | ~600 mμ | | 1.7 | 0.7 | 3.6 3.6 | 11 6.6 |
| 0.1 | 0.5 | 1.12 | 4 | 1.1 0.8 | 3.3 0.7 | 3.4 0.8 | | 12 | | | | | 14 μw | |
| 0.5 | 0.11 | 1.08 | 18 | 1.1 0.7 | 3 0.9 | 4.2 1.5 | | 19 | | | 0.4 | 0.2 | 2.5 2.5 | 6.2 5.8 |
| Al | | | | 1.4 μw | 22 μw | 80 μw | | | | | | | 1.4 μw | 25 μw |
| 0.01% | 0.28 | 1.1 | 5 | 1 0.1 | 2.2 0 | 2.5 0.2 | ¼ | 1½ | ~600 mμ | | 0.8 | 0.5 | 1.6 0.8 | 5.0 2.6 |
| 0.1 | 0.10 | 1.2 | 5 | | 2.4 0.4 | | ¼ | 3½ | | | | | | |
| 0.5 | 0.30 | 0.68 | 6.5 | | 2.1 0.3 | | ½ | 3½ | | | 0.2 | 0.5 | | 14 13 |

TABLE II. *Summary of data at 436 mμ and 546 mμ*

| Sample | 436 mμ | | | | | | | | 546 mμ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 27°C | | | | | | −49°C | | 27°C | |
| | $k$ | $n$ | $\sigma_S$ | $(\sigma_D)_\infty$ | $t_{1/2}$ min | $t_{1/2}$ min | $\sigma_S$ | $(\sigma_D)_\infty$ | $\sigma_S$ | $(\sigma_D)_\infty$ |
| Cu | | | Too small to measure | | | | | | | |
| Li | | | 25 μw | | | | | | | |
| 0.01% | 0.07 | 2.5 | 3.5 | 0 | 1 | 6 | 7.5 | 7 | 1.7 | 0.4 |
| 0.1 | 0.02 | 1 | 4.0 | 0 | 1.75 | 12 | | | | |
| 0.5 | | | 0.8 | −0.3 | 0.5 | 1.75 | | | | |
| Ga | | | 41 μw | | | | | | | |
| 0.01% | 0.0002 | 3.2 | 2 | −0.1 | 1 | 6 | 1 | 0.9 | 0.8 | 0 |
| 0.1 | | | 4.8 | 2.4 | | 13.5 | | | 0.8 | 0.6 |
| 0.5 | | | 2.8 | 2.2 | | 10 | | | 0.5 | 0.5 |
| Al | | | 42 μw | | | | | | | |
| 0.01% | 0.17 | 0.38 | 0.8 | −0.1 | 0.25 | 3.5 | | | | |
| 0.1 | | | 2.6 | 1.3 | 1 | 11 | | | | |
| 0.5 | | | 3.6 | 2.3 | 1 | 11 | | | | |

for the slow recovery of the samples over periods of 12–24 hr.) In the case of Ga samples, only a single measurable first-order process was observed, but a deviation from the first-order plot at very short times suggested the presence of an additional process with a very short time constant.

The saturation photocurrent, $\sigma_S$, usually decreased with increasing impurity concentration at 367 mμ (see Fig. 7). The only exception was the Al sample where there was some irregularity in $\sigma_S$; however, $\sigma_M$ decreased regularly with increasing impurity concentration. At the lower temperature the same regularity was observed.

At wave lengths longer than 436 mμ the same sort of regularity of $\sigma_S$ as a function of impurity was observed as at 367 mμ. At 436 mμ irregularities and inversions occurred. From Fig. 7 it can be seen that Ga and Li show an irregularity, where $\sigma_S$ does not decrease with increasing impurity. With the Al samples there is complete inversion, that is $\sigma_S$ increases with increasing impurity content.

The energy gap between valence and conduction bands in ZnO is approximately 3.2 ev, so that wave lengths longer than 385 mμ are not energetic enough to excite the width of the band. In the case of "pure" ZnO irradiated with 415 mμ light, the photoconductance shows an induction period at all intensities. A typical curve is shown in Fig. 7 in the fifth figure of column 2 (Fig. 7-II-5). In samples with 0.01% Li impurity, irradiation at 436 mμ produced a pronounced maximum in the curve where only a slight maximum was found at 367 mμ (Fig. 7-I-2 and Fig. 7-II-2). With 0.01% Ga, illumination at 436 mμ again produced a pronounced maximum, although in this case the total

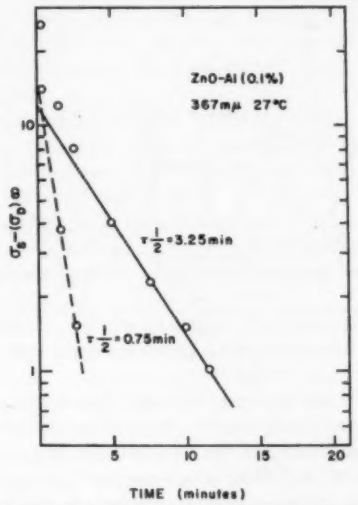



FIG. 10. Typical decay curve showing the manner of determining decay constants.

photocurrent was smaller than at 367 mμ. At still longer wave lengths these pronounced maxima disappeared again, and in both cases the photocurrents became much smaller.

The "pure" ZnO prepared in this laboratory behaved in a manner very similar to the Merck ZnO except that the Merck sample gave photoconductance to wave lengths as long as 700 mμ whereas the ZnO prepared in this laboratory cut off sharply at 425 mμ. This may be because of differences in purity of the samples since an emission spectrogram showed that the laboratory prepared ZnO was purer.

## DISCUSSION

In general the shapes of all the photoconductance curves in Fig. 7 are similar, differing only in degree, e.g., at 367 mμ they all go through a maximum and then settle down to a lower final saturation photocurrent ($\sigma_s$). All samples show a decay in photoconductance which is the sum of two first-order processes, except possibly the Ga samples.

It appears that some transfer phenomenon is associated with the absorption of light and subsequent liberation of charge carriers which may be either electrons or holes or both. At 367 mμ and low light levels (~1 μwatt) there was a very definite induction period before onset of photoconductivity. As mentioned before, "pure" ZnO at 415 mμ (Fig. 7-II-5) exhibited an induction period at all light levels. If no transfer mechanism was involved, it would be expected that photoconductivity would begin immediately upon irradiation of the sample, but the fact that a finite length of time elapsed before the photocurrent began is indicative of the transfer phenomenon. Further, in the equation $(d\sigma/dt) = kI^n$, $n$ changes with temperature. If liberation of electrons involved a direct interaction with photons, it would not be expected that $n$ would change with temperature. Even in the simplest case of the results obtained at 367 mμ and at room temperature $n$ is somewhat different from 1 indicating a complicated process. The wider departure of $n$ from unity at other conditions is an even stronger indication.

Heiland (21) also postulated an energy transfer mechanism. From calculations of quantum yield during electron bombardment he concluded that the impinging energy must be absorbed in the lattice, then transferred to centers liberating charge carriers. According to Heiland, these centers are $Zn^+$ in interstitial positions, and from a calculation based on the energy required to split off another electron and the density of absorption centers, the capture cross section of these centers for bombarding electrons would have to be some $2 \times 10^4$ times larger than that for a lattice position, an unlikely situation.

Once the light is absorbed, the energy is transferred to electron or hole liberating centers and trap forming centers. These may be identical with each other or independent of each other. If only charge carriers were produced, a continuous regular increase of photocurrent would be expected, e.g., curve AB in Fig. 11. However, after a while the curve bends and establishes an equilibrium value. Either some saturation value in the number of charge carriers available has been reached, or as many carriers are being trapped out of their conduction bands as are being excited into them. The latter is more reasonable since the absence of traps is not likely. Curve ACD represents a saturation situation. When a maximum appears in the curve (ACE) it can be interpreted in terms of still another trapping mechanism which is photochemically induced and which becomes available after a time lag. If this trapping is not restrained by a time lag, the expected curve would be like AFE. Therefore the experimentally obtained curve ACE may be interpreted with the help of at least two trapping mechanisms, one of which has a time lag and is independent of charge carrier formation. On irradiation, charge carriers are liberated and these very soon begin to be trapped since the curve begins to bend over. After a time the delayed trapping mechanism becomes increasingly important and the photocurrent is reduced to a new lower equilibrium value (curve ACE).

Another observed phenomenon can be explained with another light-induced trap mechanism. When the irradiation is cut off on samples containing Li impurity, there is a small but definite temporary increase in photocurrent before decay sets in. A more detailed general mechanism is given below, considering the charge carriers as electrons and remembering that a similar scheme can exist for holes. According to this mechanism, the incoming photon can participate in two types of processes, leading to the production of photoelectrons and to the production of traps.

*Generalized Mechanism*

Photoelectron production

| | | |
|---|---|---|
| Excitation | $A + h\nu \rightarrow A^*$ | (IV) |
| Transfer | $A^* + B \rightarrow A + B^*$ | (V) |
| Photoelectron production | $B^* \rightarrow C + e$ | (VI) |
| Trapping and immediate recovery | $C + e \rightarrow B +$ energy | (VII) |
| or | $X + e \rightarrow (X + e)$ and $(X + e) + C \rightarrow B +$ energy | (VIII) |

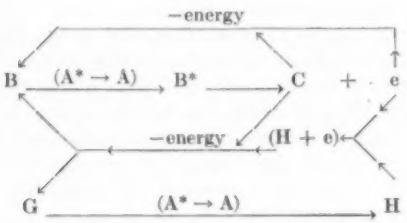
Independent trap formation

| | | |
|---|---|---|
| Trap formation | $A^* + G \rightarrow A + H$ | (IX) |
| Trapping | $H + e \rightarrow (H + e)$ | (X) |
| Recovery (after trapping) | $(H + e) + C \rightarrow B + G +$ energy | (XI) |
| or recovery of traps | $H \rightarrow G +$ energy | (XII) |

Possible subsequent trap formation

| | | |
|---|---|---|
| Trap formation... | $A^* + C \rightarrow A + D$ | (XIII) |
| Trapping and recovery..... | $D + e \rightarrow B +$ energy | (XIV) |
| or..... | $D + e \rightarrow F \rightarrow B +$ energy | (XV) |

A schematic representation of this generalized mechanism involving steps (IV) through (XII) is




In this mechanism, $H$ and $C$ or $D$ are traps for the photoelectrons.

In order to show that the generalized mechanism can be made more specific, Eqs. (XVI) through (XXVI) are given as a possibility. However, this example is only one of several possibilities, and there is not sufficient evidence at present to permit a selection of the correct mechanism from these possibilities.

*Example*

Photoelectron production

| | | |
|---|---|---|
| Excitation..... | $A + h\nu \rightarrow A^*$ | (XVI) |
| Transfer..... | $A^* + Zn_i^+ \rightarrow (Zn_i^+)^* + A$ | (XVII) |
| Photoelectron production... | $(Zn_i^+)^* \rightarrow Zn_i^{++} + e$ | (XVIII) |
| Trapping and immediate recovery..... | $Zn_i^{++} + e \rightarrow Zn_i^+ +$ energy | (XIX) |

Independent trap formation

| | | |
|---|---|---|
| Trap formation. | $A^* + Zn_i^+ \rightarrow A + Zn_L^+ + O_O^-$ | (XX) |
| Trapping..... | $O_O^- + e \rightarrow \textcircled{e}_O^-$ | (XXI) |
| Recovery..... | $\textcircled{e}_O^- + Zn_i^{++} \rightarrow Zn_i^+ + O_O^-$ | (XXII) |
| | $O_O^- + Zn_L^+ \rightarrow Zn_i^+ +$ energy | (XXIII) |

Subsequent trap formation

| | | |
|---|---|---|
| Trap formation. | $A^* + Zn_i^{++} \rightarrow A + Zn_L^{++} + O_O^-$ | (XXIV) |
| Trapping..... | $O_O^- + e \rightarrow \textcircled{e}_O^-$ | (XXV) |
| Recovery..... | $Zn_L^{++} + \textcircled{e}_O^- \rightarrow Zn_i^+ +$ energy | (XXVI) |

where $A$ = lattice; $A^*$ = excited lattice; $Zn_i^+$ = interstitial $Zn^+$; $Zn_L^+$ = lattice $Zn^+$; $O_O^-$ = anion vacancy; and $\textcircled{e}_O^-$ = electron trapped in anion vacancy (F center).

The initial discussion is confined as much as possible to the generalized mechanism. According to this, the photon excites the lattice in a fast step giving $A^*$, which subsequently passes on its energy in a thermal step to the charge liberating center $B$. The excited $B^*$ releases conduction electrons in a subsequent thermal step (VI). If $B^*$ is a reservoir requiring buildup, the mechanism will explain the observed induction period.

The probability of trapping increases with increasing concentration of conduction electrons, and the photocurrent will rise only until the rate of production and rate of removal of charge carriers become equal. The trapping could be a simple recombination according to reaction (VII), but the first-order decay processes observed suggest that a good portion of the trapping may be by a large relatively constant concentration of traps $X$ as in (VIII). The sequence of steps (IV) through (VIII) results in a curve of the form ACD with a steady-state photocurrent as at $D$.

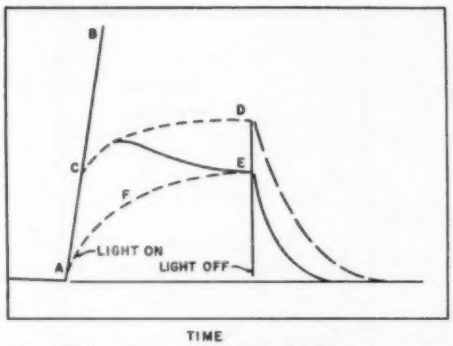



FIG. 11. Various hypothetical photoconductance curves

The fact that the photocurrent usually goes through a maximum requires a more extended interpretation. Assuming that the rate of production of photoelectrons is constant with time, then it becomes necessary to postulate a later increased rate of trapping. The fact that this lags behind the onset of illumination suggests that the traps are photochemically produced through a moderately slow thermal step. This independent formation of traps and their trapping is given in steps (IX) through (XI). Combining steps (IV)–(VIII) with steps (IX)–(XI) would result in curve of the form of ACE.

The two-trap mechanism involving one independent trap formation also helps to explain the memory of the samples. If two photocurrent curves are run consecutively, both $\sigma_M$ and $\sigma_S$ in the second curve are smaller, and in curves with a maximum the maximum becomes modified and $(\sigma_M - \sigma_S)$ is decreased. If only Eqs. (IV)–(VIII) were the trapping mechanism, then when $e$ combined with $C$ the original lattice would be reproduced. With $H$ being formed independently, the sample can have a memory, i.e., there may be many $H$ traps left after the initial decay of photocurrent. When the sample is irradiated the second time, these traps can contribute to trapping immediately. In a photocurrent curve with a maximum, the maximum tends to disappear since now a time lag is not required for some $H$ traps to be available. In other cases with small maxima, the total photocurrent is reduced.

The postulated $H$ trap formation [Eq. (XX)] requires some explanation. In ZnO, anion vacancy formation by an anion jumping into an interstitial position is unlikely; therefore, some other mechanism must be operative. It is assumed that an anion on a normal lattice site moves to the outer surface, along with its cation, by an unspecified diffusion process. The cation vacancy formed is filled by an interstitial monovalent cation, and the anion vacancy remains as such. This complicated mechanism may require an unduly long lifetime for the exciton for which no explanation can be given.

For the recovery mechanism [Eq. (XXIII)] there is surface to bulk diffusion of the ions. These involved processes are in accord with the slow buildup of traps and the memory of ZnO.

The evidence indicates that both trap formation and charge carrier formation are very temperature dependent. At −49° C the buildup of photocurrent as measured by initial slopes is very much slower than at room temperature. This indicates a strong temperature dependence for charge carrier formation. The induction period before onset of photoconductivity may also indicate an activation or thermal step.

At the low temperature in spite of the lowered rate of production of charge carriers, there is appreciable photoconductivity, in most cases larger than at room temperature, with a very small amount of decay when irradiation is cut off. This can mean either that the rate of production of traps is greatly dependent on temperature or that, instead, the rate of trapping after the traps have been formed is very dependent on temperature. If the latter part of this statement were true, then the rate of trapping should slow up but not stop until the decay of the photoconductivity is substantially complete. In fact, the trapping not only slows up but stops completely at very small values of total trapping. Hence, the trap formation mechanism must be the one which is very strongly influenced by temperature.

In the case of the Li-containing samples which exhibit a temporary slight increase in photocurrent after illumination is cut off, it becomes necessary to extend the general mechanism further. Apparently in these cases some contribution to the total trapping rate which is present in the illuminated steady state becomes inoperative in the dark. This suggests a light-induced trap formation and trapping such as that given by Eqs. (XIII)–(XV). These traps would be used almost as quickly as formed so that none would remain to contribute to the trapping in the dark during the decay. Thus the reservoir of $B^*$ could continue to supply conduction electrons for a short time in the dark so that a temporary imbalance in production and removal of conduction electrons could exist in favor of a temporary increase in their number. Later this reverts to a decay of photoconductance as the reservoir of $B^*$ becomes depleted and the trapping by other processes continues.

There seems to be some resonance phenomenon associated with the second trapping mechanism [Eqs. (IX)–(XI)]. Samples such as 0.01% Ga and 0.01% Li which show no maxima at 367 mμ show a very appreciable peaking when irradiated with 436 mμ. When irradiated with wave lengths longer than 436 mμ, the peaking again disappears. Since light absorption by the lattice is presumably confined to wave lengths below 385 mμ, the phenomena studied at longer wave lengths probably involve initial absorption of photons by portions of the ZnO which are dependent on the manner of preparation, such as impurities and other types of imperfections.

It is tempting to seek a model to describe the general mechanism in more detail. However, it is dangerous to ascribe any great reality to such models since the present state of knowledge on such a complicated system as ZnO is too meager for such detailed examination. Miller (23) has expressed a similar opinion. However, it is instructive to inquire into the more common models proposed by other authors to see to what extent they can serve to explain the experimental facts developed in this research and more particularly to see what discrepancies become obvious.

While it is not definitely known yet to what extent the bonds in ZnO are covalent or ionic, the convention of previous authors will be used, and the structure will be considered as ionic. The normal condition for strongly fired ZnO is that the composition of the compound departs from a stoichiometric ratio in the direction of excess Zn. The excess Zn is said to occupy interstitial positions and ionize to give excess electrons. These excess electrons are responsible for the electrical conductivity and cause the ZnO to be an $n$-type semiconductor. This may be represented by the equation

$$\mathrm{ZnO} \rightarrow \mathrm{Zn}_i^{+} + e + \tfrac{1}{2}\mathrm{O}_2 \qquad \text{(XXVII)}$$

or

$$\mathrm{ZnO} \rightarrow \mathrm{Zn}_i^{++} + 2e + \tfrac{1}{2}\mathrm{O}_2 \qquad \text{(XXVIII)}$$

It is well known that the electrical conductivity of ZnO increases with decreasing $O_2$ pressure. This can be easily understood with mass action concepts. An equivalent situation arises if ZnO is considered to have anion vacancies instead of excess cations in interstitial positions. This general type of model has been carried further in order to explain the probable effect of impurities on the electrical conductivity of ZnO.

If a small amount of gallium oxide is introduced as an impurity in ZnO, the process may be viewed as a replacement of a lattice Zn ion by a Ga ion. If the restriction is imposed that the oxygen ions are not disturbed and that the Ga assumes its normal valence of three, the model would predict that an additional electron would become available for conduction. Thus Ga or in general any trivalent metal oxide added as an impurity would increase the excess semiconduction of ZnO. An equivalent argument can be made by postulating that the effect of Ga is to decrease the number of interstitial Zn ions as suggested by Molinari and Parravano (9). In the case of Li and monovalent metal oxides, the model would require the replacement of two lattice Zn ions by Li and increase the interstitial Zn. Then by mass action it would be expected that the electrical conductivity would decrease.

This sort of model was used by Mollwo (12) and later by others to explain the increased conductivity which results from excitation of ZnO by light. He postulated that the interstitial Zn was in the form of $Zn^+$ and the light, after being accepted into the crystal, was used to split off the second electron giving $Zn^{++}$.

The model requires that the electrical conductivity of ZnO should be increased by addition of trivalent metal oxides and decreased by monovalent metal oxides. In this paper the electrical conductivity is designated by $\sigma_D$ (Table I). The predictions are not borne out by the present experimental data inasmuch as all of the samples containing impurities exhibit a larger $\sigma_D$ than "pure" ZnO. However the samples were fired at a relatively low temperature. This choice was made in order to minimize the normal departure from stoichiometry so that the effect due to the purposely added impurities would not be

swamped by large effects due to temperature-induced imperfections. The firing temperature may have been too low to establish predicted equilibria.

With this model and assuming equilibrium, it might be expected that the final value of the photocurrent would depend on the interstitial Zn and the interstitial Zn in turn depend on the type and concentration of impurity. Detailed examination of the present data does not show the expected trends in all cases. This situation is not surprising if a closer examination is made of the data. The value of the photocurrent at any point is a resultant of the opposing processes of excitation and trapping. It can be seen from Table I that the excitation rate, as measured by the $k$ values, not only depends on the temperature but also on the type and concentration of the impurity. The trapping also depends on temperature and impurity concentration. The photocurrent that arises from these opposing processes can have no easily predictable values.

It should also be recalled that in the case of powders, surface effects can be quite important. Adsorbed substances can also act as acceptors or donors to the bulk of the ZnO. Melnick (16) has shown the effect of adsorbed oxygen on the conductivity of sintered ZnO. In the present experiments all samples were given the same pretreatment in order to avoid further complication in the study of the effect of desired introduced impurities. Even in the case of the desired impurity, the possibility of a nonuniform distribution of the impurity on the surface and through the bulk of the samples introduces additional uncertainty in interpretation. Because of this it will be difficult to find a correlation between conductivity and catalysis with semiconductors, since conductivity is primarily a bulk phenomenon influenced to a considerable extent by the surface, while catalysis is primarily a surface phenomenon perhaps affected in part by the bulk properties of the catalyst. Correlation between photoconductivity and photocatalysis may be even more difficult to establish. In the case of samples used in this research, some correlation was found (4) between the photocatalytic efficiency for the $H_2O_2$ reaction and the initial rise of the photoconductivity at 367 m$\mu$ as measured by the values of $k$ in the second column of Table I. Details of this correlation and its significance in the photocatalytic process will be reported later with the photocatalytic studies.

## Summary and Conclusions

ZnO undergoes a memory mechanism when irradiated by light with a time constant of the order of 12–24 hr. The memory depends on the past irradiation history of the sample, and because of this any measurement is subject to some uncertainty. In the light of the present work, relations for the dependence of photoconductivity on the intensity of light found by Mollwo seem to be conditioned by his choice of procedure. Analysis of the curves for a possible mechanism for photoconductivity leads to the suspicion that the memory is caused by the formation of traps independent of charge carrier formation.

Concentration of traps is a function of impurity concentration and temperature. The rate of excitation, as measured by the $k$ values, is also a function of impurity concentration and temperature. Since both excitation and trapping appear to depend on the impurity concentration in a complex manner, the matching of the two effects at $\sigma_S$ can occur almost anywhere. Thus, it is dangerous to try to establish any regular progression in photoconductivity with impurity.

The decay of photoconductivity is largely the sum of two first order processes, and it is attractive to assign one decay constant to the decay of holes and the other decay constant to the decay of electrons. This cannot be done with any certainty, however, since it is not known which contributes the most to conductivity.

The results of this investigation cannot be reconciled with any existing model for ZnO. Since it is shown that the results depend on the impurity and the irradiation history, it appears that disagreement or agreement among previous workers is due to dissimilarities or similarities in their samples and procedures in these respects.

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# Ultraviolet Fluorescence of Some Ternary Silicates Activated with Lead

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ABSTRACT

The fluorescence and phase diagrams of the following Pb-activated ternary systems were investigated: $SrO$-$MgO$-$SiO_2$; $SrO$-$ZnO$-$SiO_2$; $BaO$-$MgO$-$SiO_2$; $BaO$-$ZnO$-$SiO_2$. Eleven new ternary silicates were identified, some of which proved to be very good base materials for Pb-activated phosphors with peak emissions ranging from 3000 to 4000Å.

Fluorescent lamps producing radiation in the region of 3000–4000Å are important for many applications, e.g., the sunlamp, which emits in the short wave-length region near 3000Å, and which is used to produce erythema. For this, radiations of 2800–3200Å are most effective with maximum response at 2970Å (1). Sunlamps are used also for the production of vitamin D from sterols. The most effective region for synthesizing vitamin D from ergosterol is 2490–3130Å (2).

A second type of ultraviolet (u.v.) lamp, the black-light lamp, emitting in the region of 3600Å, is used in a number of applications such as laundry marking, blueprinting, instrument dial illumination, window displays, etc. For the last two applications use is made of phosphors, such as sulfides, which are excited by long wave length ultraviolet.

The number of fluorescent substances which produce u.v. radiation in the region of 3000–4000Å, when excited by the Hg resonance radiation of 2537Å, is not very large. Ce-activated phosphors often fluoresce in this region, but they are less suitable in practice because of maintenance difficulties in Hg-discharge lamps and deterioration during processing. Tl-activated phosphors are more suitable. One which is used often is $Ca_3(PO_4)_2$-Tl (3, 4), which has an emission maximum at 3250Å. A more effective erythemal phosphor can be produced by partial substitution of Zn for Ca (5) which shifts the maximum to shorter wave lengths. In black-light lamps Pb-activated $BaSi_2O_5$, having an emission maximum at 3500Å, is often used (3).

The present article describes an attempt to extend the list of suitable u.v. phosphors. Since Pb-activated phosphors often have an emission in the u.v. region, most attention was paid to this activator. Because silicates appear to be the most suitable base materials for activation with Pb, several ternary systems containing $SiO_2$, one oxide of the group CaO, SrO, BaO and furthermore MgO or ZnO were investigated. Many new compounds were found, some of which appeared to be excellent base materials for Pb-activated phosphors.

## Experimental Methods

Materials used included the carbonates of Ca, Sr and Mg, ZnO, $SiO_2$ of very fine grain size,[1] and a Pb compound, usually the nitrate. A thick alcoholic slurry was made of the oxides and carbonates. This slurry was ground in a small glass jar mill and mixed with the required amount of the activator, mostly $Pb(NO_3)_2$ dissolved in water. The paste was dried and sometimes milled in a small agate runner mill. The resulting powder was fired in open alundum crucibles at 1000°–1200°C for a few hours. Often the activator was added in the form of $PbF_2$. A few percent of the fluoride of one of the basic oxides was also added occasionally. Although very little F is found in the fired material by analysis, its presence in the raw material blend often has a marked effect on the fired product. Judging from the x-ray diffraction patterns of the fired products, the reaction is more complete in the presence of a little F. Moreover, addition of a fluoride promotes crystal growth and sometimes the transition between two crystal phases. The amount of Pb added was usually of the order of 1 mole % of the basic oxides. X-ray diagrams of the fired products were made with Co-$K_\alpha$ radiation, using a North American Philips Geiger counter x-ray diffractometer.

Sufficient compositions were fired and x-ray analyzed to make it possible to identify the composition of new phases and to construct the composition diagrams for the ternary systems investigated. The identification of new compounds was in many cases greatly aided by their isomorphism with known Ca, Mg- and Ca, Zn-silicates.

### *Binary Compounds*

The following are the binary compounds which may occur and their fluorescent properties when activated with Pb:

$CaO$-$SiO_2$.—Four compounds are known: $Ca_3SiO_5$, $Ca_2SiO_4$, $Ca_3Si_2O_7$, and $CaSiO_3$. In the fired products only the last three were found. This is in agreement with the results of Carlson (6) who found that $Ca_3SiO_5$ is not stable below 1250°C and decomposes into CaO and $Ca_2SiO_4$. The $\alpha$-form of the metasilicate, or pseudowollastonite, was found predominantly. The orthosilicate occurred only in the low temperature $\beta$-form.

The fluorescence of $CaSiO_3$-Pb has already been intensively studied (7–14). With 2537Å excitation, emission bands are found at 3000 and 3500Å. Fonda and Studer (9, 11, 13) attribute the 3000Å band to $\alpha$-$CaSiO_3$-Pb and the 3500Å emission to $\beta$-$CaSiO_3$-Pb. This is disputed by

[1] Aerosil from Degussa.

TABLE I. *Spacings (d) and intensities (I) for x-ray patterns of* $SrSiO_3$ *and* $BaSi_2O_5$

| $SrSiO_3$ | | α $BaSi_2O_5$ | | | | β $BaSi_2O_5$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I |
| 5.0 | 20 | 6.9 | 10 | 2.00 | 15 | 6.8 | 20 | 2.13 | 60 |
| 3.56 | 45 | 5.6 | 10 | 1.95 | 20 | 6.4 | 5 | 2.11 | 20 |
| 3.36 | 30 | 4.75 | 10 | 1.92 | 40 | 5.8 | 5 | 2.03 | 30 |
| 2.92 | 100 | 4.05 | 100 | 1.88 | 40 | 5.5 | 5 | 1.99 | 20 |
| 2.53 | 20 | 3.85 | 15 | 1.83 | 20 | 5.0 | 30 | 1.92 | 30 |
| 2.06 | 80 | 3.55 | 50 | 1.79 | 30 | 4.3 | 30 | 1.915 | 25 |
| 1.905 | 30 | 3.35 | 40 | 1.73 | 10 | 4.0 | 95 | 1.855 | 25 |
| 1.78 | 15 | 3.27 | 35 | 1.70 | 10 | 3.8 | 30 | 1.795 | 35 |
| 1.76 | 5 | 3.17 | 75 | 1.68 | 10 | 3.40 | 75 | 1.74 | 5 |
| 1.68 | 20 | 2.88 | 35 | 1.65 | 10 | 3.32 | 95 | 1.69 | 35 |
| 1.60 | 10 | 2.78 | 45 | 1.62 | 10 | 3.25 | 35 | 1.67 | 5 |
| 1.525 | 20 | 2.61 | 25 | 1.60 | 55 | 3.09 | 100 | 1.65 | 5 |
| 1.46 | 15 | 2.51 | 20 | 1.59 | 20 | 2.98 | 10 | 1.60 | 15 |
| 1.395 | 10 | 2.41 | 5 | 1.48 | 20 | 2.89 | 10 | 1.58 | 20 |
| 1.305 | 25 | 2.35 | 35 | 1.46 | 25 | 2.72 | 75 | 1.56 | 10 |
| | | 2.26 | 60 | 1.42 | 15 | 2.58 | 25 | 1.535 | 5 |
| | | 2.22 | 80 | 1.41 | 15 | 2.54 | 5 | 1.485 | 15 |
| | | 2.16 | 25 | 1.395 | 15 | 2.50 | 5 | 1.47 | 20 |
| | | 2.07 | 40 | 1.335 | 10 | 2.40 | 10 | 1.465 | 20 |
| | | 2.04 | 35 | 1.295 | 25 | 2.32 | 20 | 1.45 | 10 |
| | | | | | | 2.23 | 60 | 1.43 | 10 |
| | | | | | | 2.19 | 25 | 1.415 | 15 |
| | | | | | | 2.16 | 40 | 1.405 | 25 |

Schulman and co-workers (12, 14) who are of the opinion that both forms of $CaSiO_3$-Pb can emit a band at 3500Å depending on the Pb content.

$SrO$-$SiO_2$.—The phase diagram of this system is known (15). Only two compounds occur, the ortho- and metasilicate. Since no x-ray data for the metasilicate were found in the literature, spacings and intensities of the x-ray lines of this compound are given in Table I.

The ortho- and metasilicate show a weak fluorescence with maxima at 3600Å and 3000Å, respectively, when activated with Pb and exposed to 2537Å radiation.

$BaO$-$SiO_2$.—All four silicates occurring in this system (15) ($Ba_2SiO_4$, $BaSiO_3$, $Ba_3Si_2O_8$, and $BaSi_2O_5$) were identified using x-ray data from the A.S.T.M. 1950 card index. In $SiO_2$-rich binary and ternary mixtures, however, extra lines were found which at first could not be identified. It appeared that $BaSi_2O_5$ could occur in two modifications. After the compound was fired at 1350°C and quenched, the x-ray pattern agreed with that of the A.S.T.M. index. Both modifications were found after firing below this temperature. When a little $BaF_2$ was added to the firing mixture, only the low temperature- or β-modification was present. The characteristic lines of both modifications are listed in Table I.

Pb-activated Ba silicates were made by Butler (16) and by Clapp and Ginther (3). The latter used Pb contents of about 1 mole % and found a weak fluorescence with maxima at 3200Å and 3750Å in the metasilicate and mesotrisilicate, respectively. Strong fluorescence with a maximum at 3500Å was obtained with Pb-activated $BaSi_2O_5$.

Butler made reasonably efficient phosphors from the metasilicate and mesotrisilicate by using Pb contents of 10 mole % or more. When more than 0.1 mole PbO/mole BaO was added to the metasilicate, a new phase appeared. The emission of these phosphors was predominantly in the blue-green region.

$MgO$-$SiO_2$, $ZnO$-$SiO_2$.—The well-known compounds $Mg_2SiO_4$ (forsterite), $MgSiO_3$ (clinoenstatite), and $Zn_2SiO_4$ (willemite) showed no appreciable fluorescence when activated with Pb. When mixtures of MgO and $SiO_2$ were fired together, the orthosilicate was formed first, even with $MgO$:$SiO_2$ ratios of one or less. To obtain the metasilicate the mixture has to be fired at temperatures above those employed here. Lines belonging to the metasilicate were found only occasionally in the x-ray diagrams of ternary mixtures.

### *Ternary Systems*

The following ternary systems were investigated: $CaO$-$MgO$-$SiO_2$; $CaO$-$ZnO$-$SiO_2$; $SrO$-$MgO$-$SiO_2$; $SrO$-$ZnO$-$SiO_2$; $BaO$-$MgO$-$SiO_2$; $BaO$-$ZnO$-$SiO_2$.

The phase diagrams of $CaO$-$MgO$-$SiO_2$ (17) and $CaO$-$ZnO$-$SiO_2$ (18) are known. The following compounds exist, all of which occur in nature as minerals: $CaMgSiO_4$, monticellite; $Ca_2MgSi_2O_7$, akermannite; $Ca_3MgSi_2O_8$, merwinite; $CaMgSi_2O_6$, diopside; $Ca_2ZnSi_2O_7$ hardystonite.

Hardystonite and akermannite are isomorphous. X-ray data for the Ca, Mg silicates are all given in the A.S.T.M. index. The spacings of hardystonite are given by Segnit (18). None of the other systems has been fully explored. Butler and Cassanos (19) made x-ray patterns of various Pb-activated $BaO$-$MgO$-$SiO_2$ mixtures and found a number of new complex silicates, but they did not establish their compositions. Moreover, they used such high Pb contents that compounds were formed which were not produced in the absence of lead. Their pattern "A" was similar to that of $BaMg_2Si_2O_7$ found here. The product obtained by firing a mixture of the molar composition

TABLE II. *X-ray data of the new 1-1-1 silicates*

| $BaZnSiO_4$ | | $BaMgSiO_4$ | |
|---|---|---|---|
| d(Å) | I | d(Å) | I |
| 4.55 | 20 | 4.55 | 40 |
| 4.05 | 20 | 4.05 | 10 |
| 3.15 | 100 | 3.15 | 100 |
| 2.64 | 75 | 2.65 | 50 |
| 2.53 | 5 | 2.53 | 10 |
| 2.46 | 15 | 2.47 | 5 |
| 2.26 | 25 | 2.25 | 40 |
| 2.19 | 25 | 2.18 | 15 |
| 2.02 | 55 | 2.03 | 40 |
| 1.97 | 30 | 1.96 | 25 |
| 1.80 | 10 | 1.72 | 15 |
| 1.72 | 15 | 1.68 | 20 |
| 1.68 | 30 | 1.63 | 5 |
| 1.64 | 15 | 1.60 | 40 |
| 1.60 | 60 | 1.58 | 15 |
| 1.58 | 20 | 1.52 | 20 |
| 1.52 | 35 | 1.385 | 10 |
| 1.485 | 10 | 1.35 | 15 |
| 1.455 | 5 | 1.315 | 10 |
| 1.435 | 5 | 1.25 | 10 |
| 1.39 | 20 | | |
| 1.35 | 20 | | |
| 1.315 | 20 | | |
| 1.275 | 20 | | |

TABLE III. *X-ray data of the new 1-2-2 silicates*

| $BaMg_2Si_2O_7$ | | | | $BaZn_2Si_2O_7$ | | | | $SrZn_2Si_2O_7$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I |
| 4.6 | 20 | 1.93 | 35 | 6.4 | 5 | 1.76 | 15 | 6.5 | 5 | 1.60 | 20 |
| 3.6 | 10 | 1.84 | 10 | 4.6 | 15 | 1.71 | 40 | 4.6 | 10 | 1.59 | 20 |
| 3.4 | 20 | 1.80 | 15 | 3.7 | 5 | 1.66 | 15 | 3.75 | 15 | 1.575 | 10 |
| 3.20 | 100 | 1.75 | 15 | 3.22 | 100 | 1.60 | 10 | 3.30 | 100 | 1.55 | 5 |
| 3.15 | 65 | 1.72 | 15 | 3.17 | 90 | 1.57 | 40 | 3.25 | 75 | 1.49 | 10 |
| 3.00 | 45 | 1.69 | 15 | 3.01 | 85 | 1.505 | 35 | 2.92 | 80 | 1.46 | 25 |
| 2.88 | 15 | 1.65 | 15 | 2.88 | 20 | 1.465 | 5 | 2.48 | 55 | 1.42 | 10 |
| 2.85 | 20 | 1.61 | 10 | 2.50 | 70 | 1.43 | 5 | 2.34 | 15 | 1.395 | 10 |
| 2.70 | 5 | 1.56 | 20 | 2.40 | 25 | 1.395 | 25 | 2.30 | 40 | 1.385 | 5 |
| 2.62 | 5 | 1.51 | 15 | 2.38 | 50 | 1.38 | 10 | 2.08 | 20 | 1.36 | 15 |
| 2.49 | 30 | 1.49 | 5 | 2.15 | 20 | 1.35 | 10 | 1.97 | 40 | 1.325 | 5 |
| 2.35 | 25 | 1.44 | 5 | 2.11 | 15 | 1.335 | 10 | 1.92 | 10 | 1.315 | 10 |
| 2.32 | 15 | 1.42 | 5 | 2.02 | 15 | 1.28 | 25 | 1.88 | 20 | 1.30 | 10 |
| 2.25 | 50 | 1.39 | 10 | 1.97 | 40 | | | 1.83 | 5 | | |
| 2.14 | 15 | 1.37 | 10 | 1.94 | 30 | | | 1.80 | 15 | | |
| 2.10 | 10 | 1.34 | 10 | 1.85 | 20 | | | 1.75 | 15 | | |
| 2.00 | 15 | 1.285 | 10 | 1.81 | 30 | | | 1.64 | 15 | | |
| 1.95 | 30 | 1.275 | 10 | | | | | 1.63 | 25 | | |

$BaO:MgO:PbO:SiO_2$ = 6:4:1:6, which according to Butler and Cassanos produces pattern "C", was shown by x-ray diagrams to be a mixture of the phases $Ba_3MgSi_2O_8$ and $Ba_2MgSi_2O_7$. In patterns "B" and "D", found by Butler and Cassanos, lines occur which are found only with products containing a large amount of Pb.

Eskola (15) tried to make Ba and Sr compounds analogous to diopside and failed. Neither were such compounds found here.

Nagy and co-workers (20) activated $Ca_2ZnSi_2O_7$ with Pb and found a strong emission band with a maximum at 3450Å on excitation with 2537Å. The best phosphor was made with excess $SiO_2$ and with a Pb content of 0.003 mole PbO/mole BaO.

Anderson and Wells (21) investigated part of the system BaO-ZnO-$SiO_2$ using Mn as an activator. On excitation with 2537Å they found a red Mn emission at 6900Å for compositions of $BaO \cdot 2ZnO \cdot ySiO_2$, where $y$ was between 1.7 and 7, preferably 2. With such compositions Larach (22) found a strong green band next to the red one on excitation with cathode rays, while the red band alone was found with a composition of $BaO \cdot ZnO \cdot 2SiO_2$. X-ray diffractions were reported to be complex and not readily interpretable in terms of luminescence.

After studying numerous x-ray diagrams of a large number of the fired ternary mixtures mentioned above, the following new compounds were identified: $SrZn_2Si_2O_7$, $Sr_2ZnSi_2O_7$, $Sr_2MgSi_2O_7$, $Sr_3MgSi_2O_8$, $BaZnSiO_4$, $BaZn_2Si_2O_7$, $Ba_2ZnSi_2O_7$, $BaMgSiO_4$, $BaMg_2Si_2O_7$, $Ba_2MgSi_2O_7$, $Ba_3MgSi_2O_8$.

The x-ray patterns of some of these new compounds could easily be indexed because of their isomorphism with known Ca,Mg- and Ca,Zn-silicates. All available x-ray data are collected in tables II–V. Sufficient information was collected from the x-ray analysis to make it possible to draw conjugation lines in the composition diagrams as shown in Fig. 1. These lines divide the ternary diagrams into a number of triangles. The final phases produced by the firing of compositions falling within these triangles are given by the apexes of the triangles.

Indicating the mole compositions in the order (CaO, SrO, BaO)-(MgO, ZnO)-$SiO_2$, it is seen that except for diopside, only the following compounds occur: 1-1-1, 1-2-2, 2-1-2, and 3-1-2.

These compounds and their fluorescence, when activated with Pb are discussed below in more detail.

*1-1-1 Compounds.*—Three compounds exist: $CaMgSiO_4$,

TABLE IV. *X-ray data of the new 3-1-2 silicates*

| Indices, hkl | $Ca_3MgSi_2O_7$ | | $Sr_3MgSi_2O_7$ | | $Ba_3MgSi_2O_7$ | |
|---|---|---|---|---|---|---|
| | d(Å) | I | d(Å) | I | d(Å) | I |
| 020 | | | 4.75 | 5 | | |
| 110 | | | 4.52 | 5 | | |
| 111 | 3.85 | 5 | 3.93 | 40 | 4.05 | 70 |
| 002 | | | 3.50 | 5 | | |
| 012 | | | 3.31 | 5 | 3.41 | 5 |
| 121 | | | 3.20 | 5 | 3.16 | 10 |
| 102 | 2.85 | 35 | 2.97 | 5 | 3.02 | 5 |
| 112; 022 | 2.72 | 50 | 2.81 | 80 | 2.93 | 95 |
| 130 | 2.66 | 100 | 2.74 | 100 | 2.81 | 100 |
| 040 | 2.31 | 15 | 2.40 | 10 | | |
| 032 | 2.27 | 15 | 2.37 | 10 | | |
| 013 | 2.21 | 30 | 2.32 | 40 | 2.43 | 35 |
| 221 | 2.16 | 20 | 2.24 | 45 | 2.31 | 55 |
| 113; 023 | 2.02 | 20 | | | | |
| 231; 042; 123 | 1.91 | 45 | | | | |
| 222 | 1.87 | 30 | 1.96 | 55 | 2.03 | 65 |
| 150 | 1.76 | 10 | | | | |
| 310 | 1.73 | 5 | 1.77 | 25 | 1.84 | 40 |
| 241 | | | 1.74 | 15 | 1.78 | 25 |
| | 1.62 | 10 | 1.67 | 5 | | |
| | 1.575 | 15 | 1.63 | 20 | 1.71 | 20 |
| | 1.555 | 15 | 1.59 | 35 | 1.64 | 50 |
| | 1.53 | 30 | 1.58 | 30 | 1.63 | 30 |
| | | | 1.545 | 5 | | |
| | 1.43 | 10 | 1.465 | 5 | 1.53 | 10 |
| | 1.39 | 10 | 1.40 | 15 | 1.46 | 20 |
| | 1.34 | 15 | 1.365 | 30 | 1.405 | 30 |
| | 1.33 | 15 | | | | |
| | | | 1.335 | 10 | 1.395 | 15 |
| | | | 1.305 | 5 | 1.35 | 20 |
| | | | 1.29 | 5 | 1.33 | 15 |
| | | | | | 1.295 | 20 |

TABLE V. *X-ray data of the new 2-1-2 silicates*

| $Sr_2ZnSi_2O_7$ | | | $Sr_2MgSi_2O_7$ | | | $Ba_2ZnSi_2O_7$ | | $Ba_2MgSi_2O_7$ | |
|---|---|---|---|---|---|---|---|---|---|
| d(Å) | I | hkl | d(Å) | I | hkl | d(Å) | I | d(Å) | I |
| | | | 5.7 | 15 | 110 | | | 5.4 | 5 |
| 5.2 | 5 | 001 | 5.2 | 5 | 001 | 3.92 | 15 | 3.93 | 40 |
| 4.35 | 4 | 101 | | | | 3.48 | 15 | 3.45 | 20 |
| | | | 4.0 | 10 | 220 | 3.16 | 100 | 3.17 | 100 |
| 3.85 | 30 | 111 | 3.80 | 10 | 111 | | | 3.02 | 10 |
| 3.59 | 5 | 210 | 3.58 | 5 | 210 | 2.92 | 30 | 2.92 | 55 |
| 3.17 | 55 | 201 | 3.18 | 30 | 201 | 2.86 | 10 | 2.86 | 20 |
| 2.96 | 100 | 211 | 2.95 | 100 | 211 | 2.72 | 40 | 2.72 | 25 |
| 2.83 | 15 | 220 | 2.84 | 5 | 220 | 2.55 | 15 | 2.54 | 10 |
| 2.60 | 15 | 002 | 2.58 | 10 | 002 | 2.39 | 20 | 2.39 | 20 |
| 2.54 | 35 | 310 | 2.53 | 25 | 310 | 2.36 | 10 | 2.36 | 10 |
| 2.48 | 10 | 221 | 2.48 | 10 | 221 | 2.21 | 10 | 2.21 | 20 |
| 2.38 | 5 | 301 | 2.38 | 10 | 301 | 2.12 | 15 | 2.12 | 10 |
| 2.32 | 2 | 112 | | | | 2.08 | 15 | 2.08 | 25 |
| | | | 2.28 | 10 | 311 | 2.05 | 15 | 2.06 | 20 |
| | | | 2.18 | 5 | 202 | | | 2.02 | 5 |
| 2.10 | 30 | 212 | 2.10 | 30 | 212 | 1.94 | 55 | 1.94 | 45 |
| 2.05 | 2 | 321 | | | | 1.91 | 25 | 1.91 | 20 |
| 2.01 | 5 | 400 | 2.00 | 10 | 400 | 1.86 | 10 | 1.85 | 20 |
| 1.95 | 15 | 410 | 1.95 | 20 | 410 | 1.78 | 15 | 1.79 | 10 |
| 1.91 | 10 | 330 | | | | 1.74 | 20 | 1.74 | 10 |
| 1.89 | 10 | 401 | 1.89 | 25 | 410; 330 | 1.70 | 40 | 1.70 | 30 |
| 1.87 | 5 | 302 | | | | 1.68 | 5 | | |
| 1.82 | 45 | 312 | 1.82 | 30 | 312 | 1.645 | 5 | 1.65 | 10 |
| 1.80 | 15 | 420 | | | | 1.585 | 10 | 1.595 | 5 |
| 1.78 | 20 | 331 | 1.78 | 20 | 331 | 1.555 | 10 | 1.555 | 15 |
| 1.73 | 5 | 003 | 1.72 | 5 | 003 | 1.505 | 15 | 1.55 | 5 |
| 1.69 | 5 | 103; 322 | 1.69 | 5 | 103; 322 | 1.49 | 20 | 1.495 | 15 |
| 1.65 | 5 | 113 | 1.65 | 5 | 113 | | | 1.485 | 10 |
| 1.59 | 10 | 203 | 1.59 | 5 | 203 | 1.46 | 10 | 1.46 | 10 |
| 1.55 | 20 | 213 | 1.56 | 20 | 213 | 1.435 | 10 | 1.44 | 5 |
| 1.53 | 4 | 332 | 1.53 | 10 | 332 | 1.405 | 15 | 1.41 | 10 |
| 1.505 | 10 | 511 | 1.505 | 5 | 511 | 1.35 | 10 | 1.345 | 5 |
| 1.475 | 10 | 223 | 1.475 | 5 | 223 | 1.315 | 5 | 1.315 | 5 |
| 1.43 | 20 | 521; 313 | 1.43 | 20 | 521; 313 | 1.295 | 30 | 1.295 | 15 |
| 1.42 | 5 | 440 | 1.42 | 5 | 440 | 1.275 | 15 | 1.28 | 10 |
| 1.375 | 5 | 441 | | | | 1.265 | 15 | 1.27 | 10 |
| 1.365 | 5 | 512 | 1.365 | 5 | 512 | | | | |
| 1.34 | 10 | 531 | 1.335 | 5 | 531 | | | | |
| 1.31 | 5 | 403 | | | | | | | |
| 1.29 | 20 | 004 | 1.29 | 20 | 004 | | | | |
| 1.275 | 10 | 620 | 1.275 | 10 | 620 | | | | |

$BaZnSiO_4$, and $BaMgSiO_4$. The last two compounds are isomorphous. This was invariably the case for corresponding Mg and Zn compounds when both occur. It is noteworthy however that the corresponding Zn analogs for some Mg compounds do not occur. For example, hardystonite and akermannite are isomorphous, while there are no CaZn compounds corresponding in composition to the other CaMg compounds, merwinite, diopside, and monticellite. From a fluorescence point of view the 1-1-1 compounds are not of interest. The Ba-containing compounds emit a broad band in the visible near 4200Å when activated with lead and excited by 2537Å. Pb-activated monticellite emits a band at 3050Å. Although this band lies in the erythemal region, the efficiency of the phosphor is too low for practical application.

*1-2-2 Compounds.*—The similarity between x-ray diagrams for $BaZn_2Si_2O_7$ and $BaMg_2Si_2O_7$ (Table III) indicates that these substances are isomorphous. This was also confirmed by the formation of an uninterrupted series of solid solutions.

$BaZn_2Si_2O_7$ is an excellent base material for activation with Pb. With low Pb contents the emission spectrum has a peak at 3030Å (Fig. 2). With higher activator content a second peak develops at 3300Å while the over-all efficiency drops. The best phosphors were obtained by firing a mixture of $BaCO_3$, ZnO, and $SiO_2$ with about 1 mole % PbO added in closed quartz crucibles for a few hours at 1000°C. The amount of BaO added preferably should be lower than indicated by the stoichiometric composition. A stoichiometric ratio of the basic constituents leads to phosphors with a comparatively low output. This is further illustrated in Fig. 3 where contour lines are drawn indicating compositions having efficiencies approximately 80% and 50% of those of the best products as measured with a 1P 21 photomultiplier in combination with Schott UG 5 and WG 7 filters, transmitting u.v. radiation between 2700 and 4000Å. The position of these contour lines is not fixed. They vary with the method of preparation. When the raw materials are mixed very thoroughly, near-stoichiometric compositions may have a higher efficiency than indicated in Fig. 3.

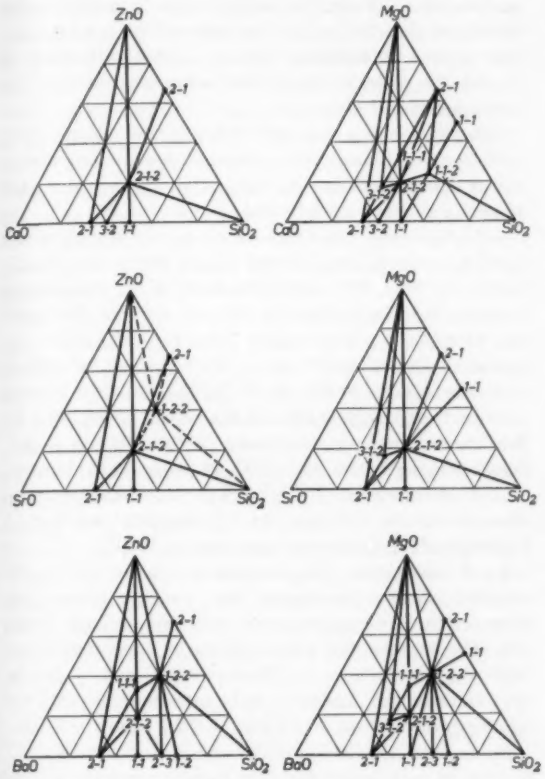


FIG. 1. Composition diagrams of the six ternary silicate ystems investigated showing conjugation lines.

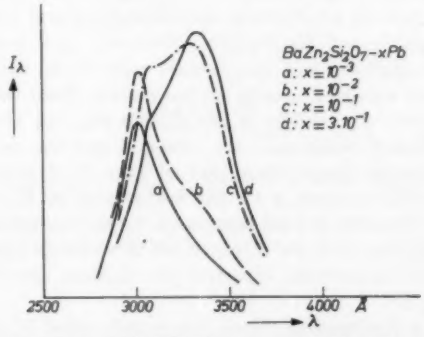


FIG. 2. Spectral distribution curves of the fluorescence of $BaZn_2Si_2O_7$-xPb fired at 1000°C and excited with 2537Å radiation.

The explanation of this effect is quite simple. When compositions near the stoichiometric point and lying in the shaded area of Fig. 3 are fired, hardly any luminescence at all is found. This shaded area is separated from the "fluorescence area" by two fairly sharply defined lines. On comparing Fig. 3 with the composition diagram of Fig. 1 it is noticed that these lines represent the boundaries between ternary mixtures containing ZnO and those without it. ZnO absorbs 2537Å very strongly, but has no appreciable fluorescence when fired with PbO under oxidizing conditions. In contrast, $Zn_2SiO_4$ and $SiO_2$ have no strong absorption for 2537Å. Therefore, their presence in the fired product is not very detrimental to the efficiency, while traces of ZnO are to be avoided. Because a solid reaction is hardly ever complete, the last remaining unreacted materials having to diffuse over increasing distances, the raw material composition must be chosen so that it is very unlikely for ZnO to remain unreacted. This is done by taking an excess of $SiO_2$.

This principle of taking an excess of the basic constituent which is comparatively harmless, in order to suppress the presence of deleterious reaction products or unreacted basic constituents, is quite generally applied in preparative phosphor chemistry [*see*, for example ref. (23–26)].

$BaMg_2Si_2O_7$ activated with Pb has a weaker emission than the corresponding Zn compound. The spectral distribution of the emission shows a maximum at 2900Å and a second maximum at 3700Å. In solid solutions of $BaZn_2Si_2O_7$ and $BaMg_2Si_2O_7$, emission shifts gradually from 3030Å to shorter wave lengths as the Mg:Zn ratio increases (Fig. 4). The efficiency is at first little affected, and may increase somewhat but it begins to drop when more than 20% of the Zn in $BaZn_2Si_2O_7$-Pb is replaced by Mg. At the same time the second 3700Å band begins to appear. This can be explained as follows.

The strong 3030Å emission in $BaZn_2Si_2O_7$-Pb is prob-

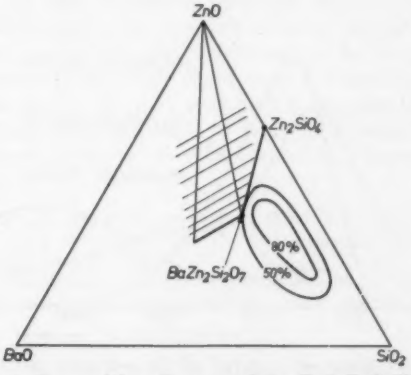


FIG. 3. Composition diagram of the BaO-ZnO-$SiO_2$ system showing contour lines for phosphors of equal brightness. The shaded area is practically nonfluorescent. The composition of the phosphors can be represented by $xBaO\,yZnO\,zSiO_2$-$r$ PbO with $r$: $(x + y + z) = 0.005$.

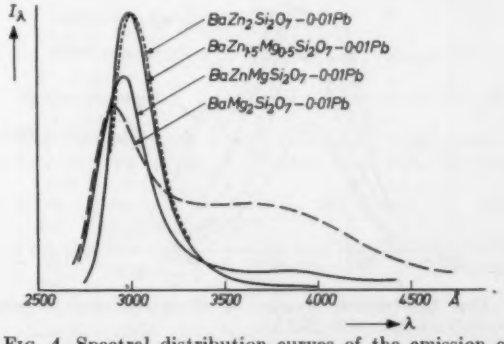


FIG. 4. Spectral distribution curves of the emission of $Ba(Zn, Mg)_2Si_2O_7$-Pb excited with 2537Å.

ably due to a transition from the $^3P$ to the $^1S$ ground state of the $Pb^{2+}$ ion. If the phosphor is to be efficient for 2537Å excitation, this wave length must lie within the excitation band corresponding to the reverse transition, preferably near its maximum. This is apparently the case with $BaZn_2Si_2O_7$-Pb. But when Mg is substituted for Zn, the emission band and presumably the excitation band move to shorter wave lengths. If the maximum of the latter moves to wave lengths shorter than 2537Å, the exciting radiation is not only less strongly absorbed, but competing transitions, such as those associated with Pb-Pb pairs, come to the fore giving rise to new emission bands, while more energy is also lost to radiationless transitions. Reflection measurements confirmed that when more than 20% of the Zn was replaced by Mg, the reflection for 2537Å began to decrease noticeably. Because of its high efficiency (quantum efficiency of the order of 90%) and the suitable spectral range of its emission, $BaZn_2Si_2O_7$ should be a very good phosphor for erythemal lamps. When lamps were made with this phosphor, however, an unexpected difficulty arose when powder came off the wall of the tube during the baking process.

It became evident from thermal analysis curves that this resulted from a reversible crystallographic transition at about 270°C. Substitution of 3% Mg for Zn moved this point to 285°C, while with more than 5% Mg added, a transition point was no longer noticeable on the thermal analysis curve. No further trouble arose from bad powder adherence after 10% of the Zn had been replaced by Mg. This partial substitution has the added advantage of moving the emission peak nearer the maximum of the erythemal sensitivity curve.

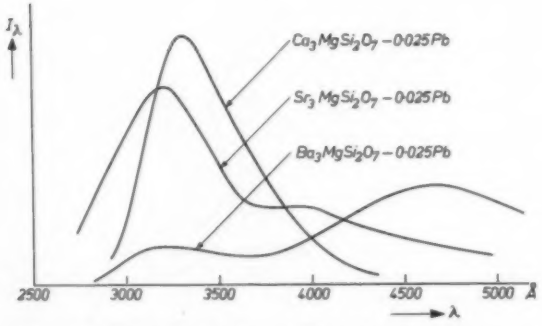


FIG. 5. Emission spectra of Pb-activated 3-1-2 compounds excited with 2537Å.

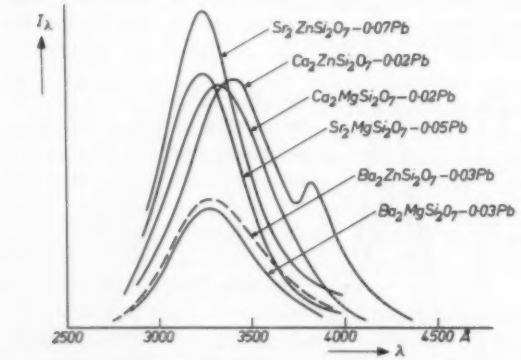


FIG. 6. Emission spectra of Pb-activated 2-1-2 compounds excited with 2537Å.

$SrZn_2Si_2O_7$ has a structure different from that of the corresponding Ba salt. The composition of this compound was at first difficult to establish mainly because the x-ray diagrams were not reproducible.

$SrZn_2Si_2O_7$ and $Sr_2ZnSi_2O_7$ were nearly always found together, even in compositions falling within the triangle formed by ZnO, $SiO_2$, and $SrZn_2Si_2O_7$ in the composition diagram. When some fluoride was added to the raw material blend, the characteristic lines for $SrZn_2Si_2O_7$ disappeared altogether. However, when a small percentage of Sr was replaced by Ba, the $SrZn_2Si_2O_7$ structure became stabilized. As much as 80% of the Sr can be replaced by Ba before a new phase appears. With more Ba added, lines belonging to the $BaZn_2Si_2O_7$ phase begin to show up.

The identification of $SrZn_2Si_2O_7$ was further complicated by the fact that its Pb emission and that of $Sr_2ZnSi_2O_7$-Pb both have a maximum at 3250Å.

*3-1-2 Compounds.*—These compounds occur only in the complex silicates containing Mg. Judging from x-ray diagrams the compounds appear to be isomorphous (Table IV). The lines of the x-ray pattern of merwinite ($Ca_3MgSi_2O_8$) were indexed by Phemister (27) and by Bredig (28), showing this substance to be orthorhombic with the following unit cell: $a_0 = 5.2$Å, $b_0 = 9.2$Å and $c_0 = 6.8$Å.

By analogy, the lines of the Sr and Ba compounds could be indexed quite easily and were found to give the following unit cells: $Sr_3MgSi_2O_8$—$a_0 = 5.4$Å, $b_0 = 9.6$Å, $c_0 = 7.2$Å; $Ba_3MgSi_2O_8$—$a_0 = 5.5$Å, $b_0 = 9.8$Å, $c_0 = 7.6$Å.

An uninterrupted series of solid solutions was found to exist between $Ca_3MgSi_2O_8$ and $Sr_3MgSi_2O_8$ and between $Sr_3MgSi_2O_8$ and $Ba_3MgSi_2O_8$. However, when mixtures of $Ca_3MgSi_2O_8$ and $Ba_3MgSi_2O_8$ were fired, the final product consisted usually of two phases. From the diagram of a 1:1 mixture it was evident that the lines for the Ca-rich phase were the strongest and the cell was considerably larger than that of pure $Ca_3MgSi_2O_8$. A substantial amount of Ca can be replaced by Ba, while little Ca seems to have been taken up by $Ba_3MgSi_2O_8$.

Regarding their fluorescence, all three compounds are of little importance. Spectral distributions are shown in Fig. 5.

*2-1-2 Compounds.*—These compounds occur in all six ternary systems investigated. X-ray diffraction data listed in Table V show that $Sr_2ZnSi_2O_7$ and $Sr_2MgSi_2O_7$ are isomorphous with $Ca_2ZnSi_2O_7$ (hardystonite) and $Ca_2MgSi_2O_7$ (akermannite) and may be considered as new members of the melilite group of silicates. The crystals are tetragonal, and the cell dimensions of both Sr compounds are about equal with $a_0 = 8.06$Å and $c_0 = 5.19$Å.

The spectral distributions of the emission of the six compounds activated with Pb and excited by 2537Å are given in Fig. 6. The Pb-activated Ca and Sr compounds are efficient phosphors with quantum efficiencies of the order of 90%. The best phosphors are again obtained when an excess of $SiO_2$ is used. Fig. 7 shows contour lines

for phosphors in the system SrO-ZnO-$SiO_2$ with about equal efficiencies. As with the ternary system BaO-ZnO-$SiO_2$, the fluorescence area is separated by sharp lines from an area of little or no fluorescence (shaded in Fig. 7) which corresponds to ternary mixtures containing ZnO. In the system SrO-MgO-$SiO_2$ an excess of MgO is not so detrimental to the efficiency, and reasonably efficient phosphors are obtained with compositions lying to the left of the lines connecting $Sr_2MgSi_2O_7$ with $Mg_2SiO_4$ in the composition diagram. Too much $Sr_3MgSi_2O_7$ must, however, be avoided since this compound is only weakly fluorescent when activated with Pb.

The Ca and Sr compounds formed an uninterrupted series of solid solutions as shown by x-ray diagrams and by the Pb emission of such solutions. Pb emission, for example, shifted gradually from 3400 to 3250Å when the Ca in $Ca_2ZnSi_2O_7$ was replaced gradually by Sr.

In both $Sr_2ZnSi_2O_7$ and $Sr_2MgSi_2O_7$, 80% of the Sr was replaced by Ba before the character of the patterns began to change, showing lines belonging to $Ba_2ZnSi_2O_7$ and $Ba_2MgSi_2O_7$, respectively. The same conclusion can be drawn from the spectral distribution of the Pb emission. When Sr was replaced by increasing amounts of Ba, the peak of the emission shifted gradually from 3250Å to longer wave lengths (Fig. 8) until it reached 3600Å with 80% replacement. With further replacement of Sr by Ba,

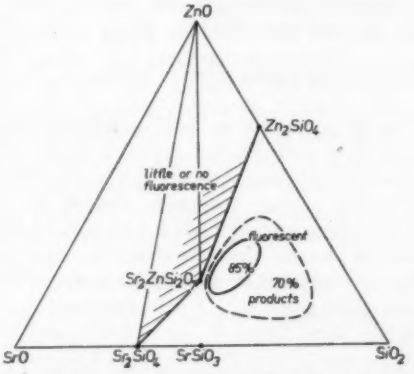


FIG. 7. Equal intensity contour lines of phosphors with composition $xSrO{\cdot}yZnO{\cdot}zSiO_2$-$r$ PbO with $r$: $(x + y + z) = 0.0025$.

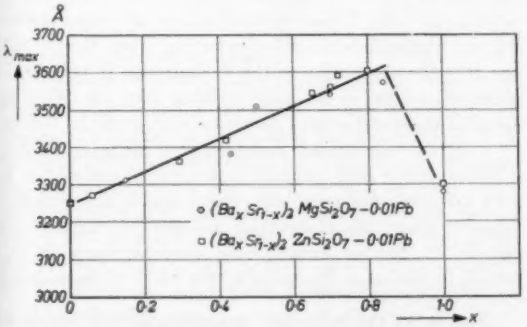


FIG. 8. Shift of the peak emission resulting from substitution of Ba for Sr in $Sr_2MgSi_2O_7$-Pb and $Sr_2ZnSi_2O_7$-Pb.

a second band belonging to $Ba_2ZnSi_2O_7$-Pb or $Ba_2MgSi_2O_7$-Pb appeared at approximately 3300Å.

All phosphors with the akermannite structure were efficient with 2537Å excitation radiation. The amount of Pb added before firing was not very critical. The optimum intensity of the 3550Å band in phosphors of the composition $10\,SrO$-$25BaO$-$20ZnO$-$45SiO_2$-$x$PbO, fired for 4 hr in an open crucible at 1050°C, was reached with $x$ of about 0.6 (0.03 mole PbO added/mole base material). When the PbO content in the raw material blend was further increased, emission intensity began to drop. Part of the PbO volatilized during preparation, depending on the firing conditions. Occasionally a loss of about 50% was found.

## Concluding Remarks

The investigation of Pb-activated ternary systems containing one oxide of the group CaO, SrO, BaO together with MgO or ZnO and $SiO_2$ led to the discovery of important phosphors with emission in the u.v. region between 3000 and 4000Å. For "sunlamps," $BaZn_{1.9}Mg_{0.1}Si_2O_7$-Pb is most useful, while for "black-light" lamps producing long wave u.v. radiation near 3600Å, $Sr_{0.6}Ba_{1.4}ZnSi_2O_7$-Pb or $Sr_{0.6}Ba_{1.4}MgSi_2O_7$-Pb are very suitable.

It is remarkable that, whereas silicates have proved to be such good base materials for the fluorescence of Pb ions, no phosphates have ever been produced with an efficient Pb emission. The reverse is true for Tl as activator. The best Tl-activated phosphors are $Ca_3(PO_4)_2$-Tl and $(CaZn)_3(PO_4)_2$-Tl. Good Tl-activated silicates have not been made so far. No explanation can be offered for this empirical rule. Many of the usual activators such as Mn, Tl, Bi, Sb, Sn, etc., were tried in the new ternary compounds. Although some of them produced a weak fluorescence, none led to phosphors of any appreciable efficiency.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1957 JOURNAL.

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# An Improvement for the Electrolytic Preparation of Aminoguanidine

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ABSTRACT

An improved method for the electrolytic preparation of aminoguanidine from nitroguanidine is described. Nitroguanidine was reduced in a suspension in 30% $(NH_4)_2SO_4$ catholyte at Pb, amalgamated Pb, Zn, spongy Zn coating Pb, and Fe at a current density of 3–10 amp/dm$^2$ at about 10°C. A yield above 80% aminoguanidine was constantly obtained. Among these cathodes, Pb was the most favorable one, giving above 85% yield.

Some considerations are also given to the reasons for getting a good yield.

Electrolytic preparation of aminoguanidine was first claimed in yield as high as 80% by reduction of nitroguanidine suspended in a dilute solution of $H_2SO_4$ using a Sn cathode (1). Lieber and Smith reported that this work has not yet been confirmed (2).[1]

Recently, the authors carried out this electrolytic reduction and obtained aminoguanidine in about 60% yield by use of a concentrated solution of nitroguanidine in 80% $H_2SO_4$ with cathodes such as Pb, amalgamated Pb, or Sn (3). Similar work was reported by Shreve and Carter (4). In this process, a suspension of nitroguanidine in 8–10% $H_2SO_4$ was reduced using a Hg cathode to give aminoguanidine in yields as high as 50–60%.

Spreter and Briner (5) also suggested a mechanism for the electrolytic reduction of nitroguanidine in dilute $H_2SO_4$. A yield of 75–80% was recorded for the Sn cathode. However, only about 1.00 g of the sample suspended in 230 cc 5% $H_2SO_4$ was used as catholyte, so these results did not seem to be applicable on an industrial scale.

As the result of these early works, it seemed that in practice the yield of aminoguanidine could not exceed 50–60% of theoretical if an acid medium such as $H_2SO_4$ were used as catholyte.

Sugino and Yamashita also studied the reaction mechanism (3). Nitroguanidine, on electrolytic reduction in a solution of strong $H_2SO_4$ at a Pb cathode, yielded aminoguanidine and guanidine as the main products. The latter compound was probably not a final reduction product, but an acid hydrolytic product of nitrosoguanidine which might be the primary reduction product. It was also found that nitroguanidine could not be reduced to aminoguanidine at Pt under the same conditions, and guanidine was the main product in this case. On the other hand, reduction potentials ($E_{\frac{1}{4}}$) of nitroguanidine and nitrosoguanidine were found to be −0.67 v and −0.56 v (vs. S.C.E., conc. $2 \times 10^{-4}$ mole/l, *p*H 3.0), respectively, by the polarographic method as shown in Fig. 1.[2]

This led to the conclusion that both compounds must be reduced electrolytically not only at Pb or Hg cathodes, but also at Pt or Fe cathodes, regardless of the current or material yield. It seemed that the reason for not obtaining aminoguanidine at cathodes having a low H overvoltage was the superiority of the decomposition velocity of nitrosoguanidine in an acid medium over its reduction speed at these cathodes. This assumption could be verified by a careful experiment. Suspension of nitroguanidine in a dilute acetic acid solution was used as catholyte. At a Pt cathode, aminoguanidine was found in the reduction product after the theoretical amount of current was passed. By further experiments, however, even in this catholyte and at a Pb cathode, the yield of aminoguan-

[1] Later the same authors published a paper reporting 75% yield of aminoguanidine with a current efficiency of 38% using 5% $H_2SO_4$ and an amalgamated Pb cathode (6).

[2] This is not the reproduced polarograms from the previous paper, but those newly measured. In a previous paper (3), the reduction potentials were shown not as $E_{\frac{1}{2}}$, but as so-called decomposition potential vs. $\frac{1}{10}$ N.C.E.

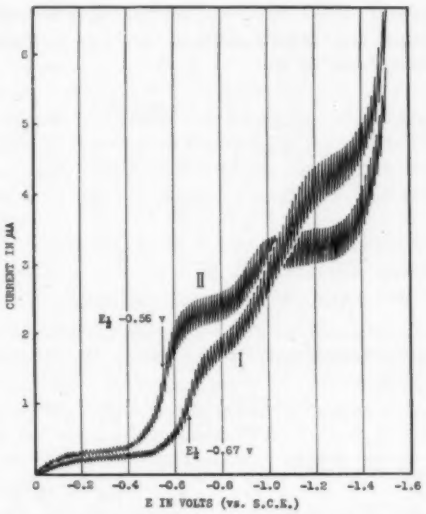


FIG. 1. Polarograms of nitroguanidine (curve I) and nitrosoguanidine (curve II) in 0.1 *N* KCl with added HCl (*p*H 3). The *m* and *t* values ($h$ = 44 cm): *m*, 1.41 mg/sec; *t*, 3.3 sec; 22°C.

idine did not reach a satisfactory value from a practical point of view.

The problem was studied further in order to find a better catholyte which would prevent decomposition of nitrosoguanidine and facilitate its reduction to aminoguanidine; an $(NH_4)_2SO_4$ solution proved the most suitable catholyte. In a caustic alkaline medium,[3] very poor yield of aminoguanidine was obtained because of decomposition of nitroguanidine itself and other intermediate reduction products. So it seemed interesting that the reduction proceeded smoothly without side reactions in an ammoniacal solution in the presence of an acid radical.

## Apparatus and Procedure

*Material used.*—The sample of nitroguanidine used in these reduction studies was prepared by dehydration of guanidine nitrate by the usual method. It melted with decomposition at 240°–245°C.

*Catholyte.*—The catholyte of this reduction consisted of a suspension of nitroguanidine in 30% $(NH_4)_2SO_4$ solution. The catholyte became ammoniacal during electrolysis, and nitroguanidine was dissolved gradually in the catholyte during electrolysis.

*Apparatus.*—The apparatus is shown in Fig. 2. A 200 cc beaker served as the cell. A porous cylindrical pot (unglazed earthenware) separated the anode space from the surrounding cathode chamber. The cathode consisted of a metal sheet bent into the form of a cylinder which stood in the beaker and encircled the porous pot (active area: 1 $dm^2$ except runs 13, 15, and 16). A thermometer was inserted within the cathode space. The catholyte was stirred slowly by a glass stirrer. The anode was a Pb sheet or a Pt plate.

[3] This medium was suitable to obtain nitrosoguanidine by the electrolytic reduction of nitroguanidine, as described in footnote [4].

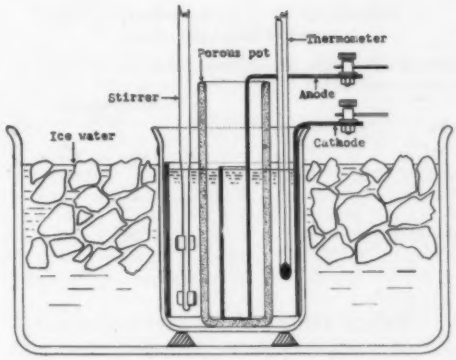


FIG. 2. Electrolytic cell

*Duration of electrolysis.*—All electrolyses except those in Table IV were conducted until reduction was complete, as indicated by the disappearance of suspended nitroguanidine which resulted in a clear solution. Three runs in Table IV were carried out with a constant amount of current.

*Determination of the products.*—After reduction, aminoguanidine was determined by Jamieson's $KIO_3$ method (7) which gave reliable results. This determination was thought to be influenced by the presence of nitrosoguanidine and also hydroxylamine or guanylhydroxylamine, the formation of which might be expected. But such compounds did not exist in the final reduction product, so the substance having the reducing power was aminoguanidine only. The accuracy of this method was checked by direct determination of aminoguanidine as bicarbonate by passing carbon dioxide in the reduction product. Good agreement was observed between the two methods. In a large experiment using 50 g nitroguanidine at a time, aminoguanidine was determined directly as aminoguanidine bicarbonate.

Guanidine was determined as picrate after removal of aminoguanidine as bicarbonate.

## Results and Discussion

*Influence of cathode materials.*—Material yields and current efficiencies for the reduction of nitroguanidine at various cathode materials are shown in Table I.

It is seen that Pb was the most effective cathode mate-

TABLE I. *Reduction of nitroguanidine at various cathodes*

Anode: Pt; anolyte: 10% $H_2SO_4$ (60–65 cc); catholyte: 5.20 g nitroguanidine suspended in 100 cc 30% $(NH_4)_2SO_4$; amperage: 3; current density: 3 amp/$dm^2$; temp: 8°–10°C.

| Run No. | Cathode | Duration of run (hr) | Aminoguanidine (as free base) yield | | Current efficiency (%) |
|---|---|---|---|---|---|
| | | | (g) | (%) | |
| 1 | Pb | 4.5 | 3.14 | 85 | 51 |
| 2 | Amalgamated Pb | 4.0 | 3.11 | 84 | 56 |
| 3 | Zn | 4.0 | 2.98 | 80 | 54 |
| 4 | Fe | 4.5 | 2.98 | 80 | 48 |
| 5 | Sn | 4.5 | 2.14 | 58 | 34 |
| 6 | Ni | 4.5 | 1.79 | 48 | 29 |
| 7 | Cu | 4.5 | 0.90 | 24 | 15 |

TABLE II. *Effect of temperature on the yield of aminoguanidine*

Cathode: Pb; other conditions: same as in Table I.

| Run No. | Temp, °C | Duration of run (hr) | Aminoguanidine yield | | Current efficiency (%) |
|---|---|---|---|---|---|
| | | | (g) | (%) | |
| 8 | −4 to −2 | 5.65 | 3.22 | 87 | 41 |
| 9 | 8–9 | 5.0 | 3.17 | 86 | 46 |
| 10 | 14–16 | 4.0 | 2.99 | 81 | 54 |
| 11 | 24–26 | 3.5 | 2.81 | 76 | 58 |

TABLE III. *Effect of current density on yield of aminoguanidine*

Cathode: Pb; other conditions: same as in Table I; 3 amp.

| Run No. | Cathodic current density (amp/dm²) | Duration of run (hr) | Aminoguanidine yield | | Current efficiency (%) |
|---|---|---|---|---|---|
| | | | (g) | (%) | |
| 12 | 3 | 4.3 | 3.22 | 87 | 54 |
| 13 | 10 | 5.5 | 3.20 | 86 | 42 |

rial, and at this cathode, the yield of aminoguanidine reached about 85%. Amalgamated Pb gave almost the same result as Pb. Zn and Fe seem to be the next best cathode materials, and an 80% yield of aminoguanidine was obtained at these cathodes. At Sn and Ni cathodes, the yield of aminoguanidine was about 60% and 50% respectively. Cu was the most inefficient cathode for preparing aminoguanidine. At these cathodes, large amounts of guanidine and $NH_3$ were obtained with aminoguanidine. In view of these results, all subsequent experiments were carried out with Pb cathodes.

*Influence of temperature.*—The influence of temperature on the yield of aminoguanidine is shown in Table II. Conditions of electrolysis were the same as in Table I.

Temperatures below 8°–10°C gave the highest aminoguanidine yields, but even at 25°C, the yield was very little less. This fact is very important from a practical point of view, because in the usual catholyte using $H_2SO_4$, the temperature rise showed marked unfavorable effect on the aminoguanidine yield.

*Influence of current density on aminoguanidine yield.*—In an attempt to compare the influence of current density on the yield of aminoguanidine, two runs were made at current density of 3 amp/dm² and 10 amp/dm². Results are shown in Table III.

The same yield of aminoguanidine was obtained at 10 amp/dm² as at 3 amp/dm².

*Influence of current density on current efficiency.*—Current efficiencies for the reduction at several current densities are shown in Table IV. All electrolyses in Table IV were made with the same amount of current (1.5 amp-hr).

There is a decrease of current efficiency as current density changes from 3 to 20 amp/dm². Since the increase of current density minimizes the duration of electrolysis for the same cathode area with the same yield of aminoguanidine as described above, it should be possible, in practice, to determine the current density which will give the maximum economical efficiency.

TABLE IV. *Effect of current density on current efficiency*

Cathode: Pb; other conditions: same as in Table III; duration of run, 1.5 hr.

| Run No. | Cathodic current density (amp/dm²) | Aminoguanidine yield | | Current efficiency (%) |
|---|---|---|---|---|
| | | (g) | (%) | |
| 14 | 3 | 1.12 | 30 | 54 |
| 15 | 10 | 0.97 | 26 | 47 |
| 16 | 20 | 0.78 | 21 | 38 |

TABLE V. *Large scale experiments*

Anode: Pb; anolyte: 200 cc 10% $H_2SO_4$; catholyte: 52.0 g nitroguanidine suspended in 450 cc 30% $(NH_4)_2SO_4$ solution.

| Run No. | Cathode | Amperage (amp) | Current density (amp/dm²) | Voltage (v) | Temp, °C | Time (hr) |
|---|---|---|---|---|---|---|
| 1′ | Pb | 10 | 4 | 4.8–4.9 | 10 | 12 |
| 2′ | Fe | 10 | 3.7 | 4.6 | 10–12 | 12 |
| 3′ | Pb (base)–Zn (surface) | 15 | 15 | 6.5–6.6 | 11–13 | 8.4 |

| Run No. | Yield of aminoguanidine bicarbonate | | | | | Current efficiency (%) |
|---|---|---|---|---|---|---|
| | crystal | | in solution (g) | total | | |
| | (g) | purity | | (g) | (%) | |
| 1′ | 56.3 | 99.0 | 2.5 | 58.2 | 86 | 57 |
| 2′ | 52.8 | 97.8 | 2.1 | 53.7 | 79 | 53 |
| 3′ | 54.3 | 97.7 | 2.2 | 55.2 | 81 | 52 |

*Result of a large experiment using 50 g nitroguanidine.*—With reference to the results obtained by the above runs, a set of experiments was performed using 50 g nitroguanidine at once in order to confirm the applicability of this method to the practical electrolysis.

The apparatus used in this experiment was similar to that described above, but had somewhat larger dimensions (1 l beaker, active area of cathode: Run 1 and 2, 2.5 dm², Run 3, 1 dm²).

When reduction was complete the *p*H of the catholyte was adjusted to 8 by passing $CO_2$, and the catholyte was allowed to stand overnight. The precipitate of aminoguanidine bicarbonate was filtered, washed, dried below 50°C, and weighed. By this procedure, 96–97% of aminoguanidine in the catholyte was crystallized out as bicarbonate. Results are shown in Table V.

At Pb cathodes, the yield was 86% of theoretical with the current efficiency of 57% which was almost the same as those obtained in the small experiment. Also at Fe cathodes, the yield was about 80% with 53% current efficiency, but the resulting aminoguanidine was somewhat colored. Use of spongy Zn-coated Pb[4] as cathode seemed to be favorable because of the application of high current density which reduced the time required, but little decrease of current and material yield resulted.

*Formation of guanidine.*—It was shown in Table I that at cathodes such as Ni and Cu the yield of aminoguan-

[4] This cathode was first applied to the electrolytic reduction of nitrobenzene to hydrazobenzene in alkali emulsion by K. Sugino and T. Sekine. The detail was described in that paper to be published.

idine was only 48 and 24% of theoretical, respectively. In these cases, guanidine and $NH_3$ were the main products. Table VI shows comparative yields of aminoguanidine and guanidine at Pb and Cu cathodes.

The formation of guanidine is seen to result from direct reduction of nitrosoguanidine and not from hydrolysis of it as in acidic medium, accounting for the observations described below. Cu seems to accelerate this reaction especially.

*Some considerations about reasons for obtaining aminoguanidine in good yield in ammonium sulfate catholyte.*—In order to clarify the reasons for the above results, the following experiments were carried out.

*Isolation of nitrosoguanidine—the intermediate product.*—It is seen that nitrosoguanidine is the primary product in this reduction, because the catholyte becomes yellow in the earlier stage of the electrolysis. Indeed, it could be detected when the reduction was carried out at 45°C. An example follows:

Anode, Pt; anolyte, 30% $(NH_4)_2SO_4$; catholyte, 5.2 g nitroguanidine suspended in 100 cc 30% $(NH_4)_2SO_4$; cathode, lead; amp, 7; current density, 7 amp/dm²; temp, 45 ± 2°C; duration of run, 35 min.

After reduction, unconverted nitroguanidine was separated out by cooling the deep yellow catholyte at 5°C. After removal of nitroguanidine by filtration, the filtrate was allowed to stand for 2 hr at 5°–10°C. Yellow powder of nitrosoguanidine was then separated out slowly from the filtrate. It was filtered and dissolved in 10 cc 3% HCl, to remove nitroguanidine. A small amount of undissolved matter was removed by filtration, and the resulting solution was neutralized with $NH_3$. Pure nitrosoguanidine was precipitated out. It was filtered, washed with water, methanol, and ether, air-dried, yield 0.10 g. Calc'd for $CH_4N_4O$: N, 63.6%. Found: N, 63.3%.

Identity was further confirmed by the precipitation of a brown Cu complex salt by adding an ammoniacal solution of $CuSO_4$ to an aqueous solution of nitrosoguanidine thus obtained.

*Hydrolysis of nitrosoguanidine.*—This compound was found not to hydrolyze to guanidine in ammoniacal catholyte at low temperature under the same conditions as in the electrolysis.

Sample: 4.40 g of nitrosoguanidine[5] suspended in a solution prepared from 10 g $(NH_4)_2SO_4$, 10 cc 28% $NH_3$, and 90 cc water. For 4 hr stirring at 10°C no guanidine was obtained; at 30°–33°C, only 7% guanidine was formed. Copper or copper ion was proved to have no effect on hydrolysis of nitrosoguanidine.

It is well known that, in acidic medium, nitrosoguanidine is hydrolyzed very rapidly to guanidine and other products (9).

Nitroguanidine and aminoguanidine did not hydrolyze to guanidine under the same conditions.

*Reduction of nitrosoguanidine.*—Then, nitrosoguanidine was reduced at a Pb cathode, the results of which are shown in Table VII.

[5] The sample of notrosoguanidine was prepared in yield as high as 45–50% by the electrolytic reduction of nitroguanidine in a caustic alkaline catholyte. The details will be published in a separate paper (8).

TABLE VI. *Reduction of nitroguanidine at* Pb *and* Cu *cathodes*

Catholyte: 10.4 g (Pb) and 5.2 g (Cu) nitroguanidine suspended in 100 cc 30% $(NH_4)_2SO_4$ solution; other conditions: same as in Table I.

| Run No. | Cathode | Duration of run (hr.) | Aminoguanidine yield | | Guanidine picrate yield | |
|---|---|---|---|---|---|---|
| | | | (g) | (%) | (g) | (%) |
| 17 | Pb | 8.5 | 6.27 | 85 | 2.18 | 7.6 |
| 18 | Cu | 4.5 | 0.78 | 21 | 9.40 | 65 |

TABLE VII. *Reduction of nitrosoguanidine at* Pb *cathode*

Catholyte: 4.40 g (Run 19), 8.80 g (Run 20) nitrosoguanidine suspended in 100 cc 30% $(NH_4)_2SO_4$; other conditions: same as in Table I.

| Run No. | Duration of run (hr) | Aminoguanidine yield | | Guanidine picrate yield | |
|---|---|---|---|---|---|
| | | (g) | (%) | (g) | (%) |
| 19 | 3.0 | 2.94 | 79 | 0.61 | 4.2 |
| 20 | 5.5 | 5.82 | 79 | 1.59 | 5.5 |

These results almost agreed with those of the reduction of nitroguanidine at Pb in Table VI.

The reduction of nitrosoguanidine at a Cu cathode under the same conditions gave a considerable amount (40 ~ 50%) of guanidine with aminoguanidine just the same as the reduction of nitroguanidine at the same cathode.

*Behavior of aminoguanidine toward reduction in* $(NH_4)_2SO_4$ *catholyte.*—Aminoguanidine itself was found not to be further reduced electrolytically to guanidine and $NH_3$ at Pb or Cu cathode under the same conditions.

From these observations, it seems that the relative stability of nitrosoguanidine toward hydrolysis in ammoniacal catholyte is one of the reasons for obtaining aminoguanidine in good yield at Pb or other suitable cathodes. Another reason may be the existence of sulfate in the catholyte. This combines with aminoguanidine to stabilize it, because aminoguanidine is a stronger base than ammonia. This assumption was supported by the fact that this process was not applicable to the electrolytic reduction of nitrourea to semicarbazide or to the reduction of nitroguanylurea to aminoguanylurea (10). In the latter cases, the products are a weaker base than $NH_3$, so that sulfate cannot combine and stabilize them during electrolysis.

## Conclusions

1. A greater than 80% yield of aminoguanidine was constantly obtained in $(NH_4)_2SO_4$ catholyte at Pb, amalgamated Pb, Zn, spongy Zn coated Pb and Fe. Among these cathodes, Pb is the most favorable one, giving above 85% yield.

2. Cu is the most inefficient cathode for the preparation of aminoguanidine in this catholyte. At this cathode, guanidine and $NH_3$ were the main products of the reduction.

3. The reduction of nitroguanidine in $(NH_4)_2SO_4$ catholyte seems to be the true electrochemical reaction accounting for the polarographic wave and not the chemical reaction with soluble electrode as suggested by Briner and co-worker in $H_2SO_4$ catholyte.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1957 JOURNAL.

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# Structure of Chemically Deposited Nickel

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ABSTRACT

An analysis was made of the structure of the Ni deposit produced by the catalytic Ni reduction process. X-ray and electron diffraction revealed that the Ni deposit was an amorphous solid. The structure appeared to be unrelated to and independent of the nature of the substrate and thickness of the deposit.

Metallographic examination revealed a dense material, free of voids, and perfect conformity to the substrate surface profile. Etching produced a lamellar structure, the variation in etching intensity being interpreted as variations in dissolved P. In platings, the lamellae lay parallel to the plane of the substrate. Growth faults were observed traversing the thickness dimension from substrate surface irregularities. The amorphous structure reverted to a crystalline phase mixture of Ni and $Ni_3P$ at low temperatures with a large heat evolution.

*Basic reactions of chemical* Ni *coating processes.*—The Kanigen[1] Ni plating process is based on catalytic reduction of Ni ions in the presence of hypophospite ions.

The hypophosphite anion in aqueous medium is oxidized to the phosphite ion with evolution of H, the rate being a function of temperature and hypophosphite concentration. This oxidation takes place spontaneously (homogeneous reaction) in alkaline solution at elevated temperature, while, under neutral or moderately acid conditions, the presence of a catalytic metal belonging to Group VIII of the periodic system, particularly Pd or Ni, is required (catalytic heterogeneous reaction). Wieland and Winkler (1) assumed, on the basis of organic analogies, a catalytic de-hydrogenation of the hypophosphite molecule according to the equation:

$$H(H_2PO_2) \xrightarrow[\text{Catalyst}]{-2H} HPO_2 + H_2O \rightarrow H_2(HPO_3) \quad (I)$$

| Hypophosphorous acid | Metaphosphorous acid | Orthophosphorous acid |
|---|---|---|

In a study of the mechanism of catalytic hypophosphite oxidation, Franke and Moench (2), using D as a tracer in lieu of H atoms, confirmed Wieland's hypothesis, and demonstrated that hypophosphite did not actually "decompose" the water molecule.

If the aqueous alkaline hypophosphite solution is relatively concentrated and contains cations of heavy metals which can be reduced, such as Ni, Co, Cu, Bi, Ag, Pd, Rh, Au, etc., a dark spongy or lustrous precipitate forms

[1] Kanigen is a trade name used by General American Transportation Corp. and its licenses to identify the Ni deposit or coating which is the product of a catalytic Ni reduction process.

when the solution is heated. In the case of Ni and Co, solid metal-phosphorus alloys are formed.

Furthermore, if the metal cation present in the neutral or slightly acid hypophosphite solution is that of a catalytic metal such as Ni, and a catalytic solid surface is immersed simultaneously, deposition will be limited to said surface and will continue until the solution is depleted of hypophosphite ion or of the metallic cation. The gross equation was written by Brenner and Riddell (3):

$$NiCl_2 + NaH_2PO_2 + H_2O \xrightarrow{\text{Catalyst}} Ni + NaH_2PO_3 + 2HCl \quad \text{(II)}$$

The reduction of Ni ions appears to be caused by atomic (nascent) H adsorbed as a condensed layer on the catalytic surface. Concurrently, there is a secondary reaction among the hypophosphite (and probably the phosphite) ions, atomic H, and Ni cations, resulting in the formation of Ni phosphide (possibly with a phosphonium salt as intermediate compound).

The basic reactions can be expressed tentatively by the following:

$$n(H_2PO_2)^- \xrightarrow[\text{Catalyst}]{-2nH} n(PO_2)^- \quad \text{(III)}$$

$$2H^+ \rightarrow H_2 \quad \text{(IV)}$$

$$(PO_2)^- + H_2O \rightarrow H(HPO_3)^- \quad \text{(V)}$$

$$Ni^{++} + 2H \xrightarrow[\text{Catalyst}]{} Ni^\circ + 2H^+ \quad \text{(VI)}$$

$$(H_2PO_2)^- + 3Ni^{++} + 7H \xrightarrow[\text{Catalyst}]{} Ni_3P + 5H^+ + 2H_2O \quad \text{(VII)}$$

From the catalytic surface of the solid, a stream of H bubbles escapes, and deposition of a high Ni-low P alloy takes place. This alloy is itself a catalyst, so that the coating thickness will grow constantly for a certain time period, which is limited by the *p*H decrease and instantaneous ion concentration. As can be seen from Eq. (VI) and (VII), the *p*H of the bath will drop as the reaction proceeds.

*General American processes.*—The character of the basic reaction and the drawbacks of the Bureau of Standards method, including published modifications thereof, indicated the direction research and development work should take for industrial production.

The principal disadvantages of the original Bureau of Standards process (3) are: slow rate of deposition, lack of stability of the bath in continuous operation, dull and even rough plating when the bath is used for longer periods, nonhomogenous deposits in the vertical direction, and relatively high cost (mainly because of a short useful life of the coating solution).

Study of a simple acid bath containing Ni and hypophosphite ions and a buffer such as sodium acetate revealed that in order to obtain both maximum deposition rates and optimum plating quality, reagent concentrations, ion ratios, and initial *p*H are critical (4).

It was discovered that the addition of short-chain aliphatic dicarboxylic acids and/or soluble fluorides ("exaltants") will substantially raise the coating rate (5, 6).

If a chemical coating bath is to be used in a production plant, it is very important to increase the span of its useful life. The limit of phosphite concentration, at which nickel phosphite precipitates, can be raised from 0.07 to about 1.0 mole/l by judicious addition of certain Ni chelating compounds, provided an "exaltant" is present to keep the deposition rate at a practical level.

The problem of bath stability is among the most serious in an industrial plant. The first visible result of excessive bath lability is the appearance of foam (due to excess H) and finely dispersed "black precipitate" (Ni-P alloy), which, because of its enormous area, acts as a very large catalytic surface. It was found that certain inhibitors, if used in properly adjusted amounts, act selectively (mainly because of geometric factors) on the suspensoids (active nuclei) making them noncatalytic, while they reduce only very slightly the rate of Ni-P deposition on the solid body to be coated.

In addition to the above improvements in bath composition, which are essential for industrial production, new principles were established relating to continuous operation and plant design, based on the requirements of catalytic reduction (7), as follows: (*A*) Because the plating rate is an exponential function of temperature, the highest possible operating temperature (below the boiling point of the solution) is desirable in order to obtain maximum speed of deposition. (*B*) It is necessary to feed continuously the consumable reagents (Ni, hypophosphite, hydroxyl ions, and stabilizer) in order to maintain maximum coating rate, optimum quality, and have the coating composition constant in a direction perpendicular to the catalytic surface. The regeneration chemicals can be added as concentrated solutions or powdered solids (to avoid bath dilution) if the bath is first cooled to a relatively low temperature (8, 9) (to prevent bath decomposition). (*C*) It is possible to meter the regeneration chemicals controlled by *p*H measurements because the various reactions in the bath are interrelated [see Eq. (III)–(VI)], and there is a fixed proportionality between the quantity of hydroxyl ions required to keep the *p*H constant, the weight of Ni-P deposited, and the amount of hypophosphite consumed.

The requirements stated above have been incorporated into the industrial Kanigen coating system, which can be described schematically as follows (7, 8, 10). The bath is prepared and kept at a relatively low temperature of about 130°F. It flows into the coating tank through a heat exchanger, which raises its temperature to 208°–210°F. From the coating tank, it is pumped into a regeneration vessel where reagents are added in controlled amounts to bring the solution's components back to their original concentration. The liquor then flows through a filter and circulates back through the heater to the coating tank.

The plant is designed in such a manner that most of the handling (pumping, filtration, etc.) of the bath is done in the "cold" section.

In many cases, when the interior of a large vessel is to be coated, the part itself becomes the plating tank.

The bath can be used until such time as the concentration of phosphite ions builds up to the point where nickel phosphite begins to precipitate. A procedure has been developed (patent pending), with several improvements

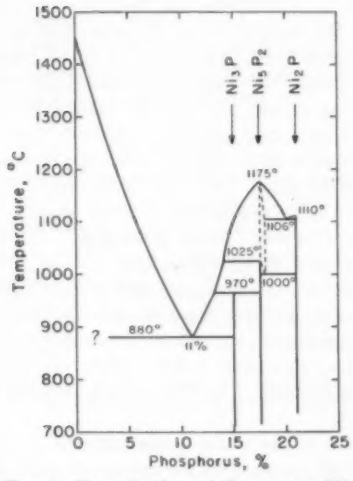


FIG. 1. Constitution of the system Ni-P

under study, which allows removal of phosphites and reclamation of the used bath without introducing any foreign ions.

Pretreatment of parts for coating by chemical reduction is essentially the same as for electrolytic plating. Because no electrical equipment is needed in a chemical coating plant, soak-cleaning procedures are preferred. Some special techniques had to be developed or adapted for deposition of Ni on certain noncatalytic metals, alloys, and nonmetals.

## Composition and Constitution

The chemically reduced metal coating was primarily metallic Ni containing 7–10 w/o P. Analyses were conducted for both metallic and nonmetallic impurities. The material used for this purpose was a quantity of deposited foil about 10 mils thick which had been stripped from panels specially treated to permit easy stripping. The foil was bright, smooth, and apparently free of surface imperfections.

Spectrographic analysis for heavier elements showed only trace amounts of Al, Ca, Fe, Mg, Pb, and Si. The term "trace" is a qualitative definition for less than 0.1% and probably less than 0.01%. Analyses for what are normally considered interstitial elements yielded the following results: C, 0.04%; O, 0.0023%, N, 0.0005%, H, 0.0016%.

The form of the phase diagram was originally mapped out by Konstantinov (11) in 1908; no work has been reported since. His version of the diagram is shown in Fig. 1. There is no information on the solid solubility of P in Ni, although from considerations of size factor and relative electro-negativity, it might be expected to be of the order of 5 w/o.

The low melting eutectic is a phase mixture of Ni solid solution and $Ni_3P$. The structure of the $Ni_3P$ phase was reported by Nowotny and Henglein (12) as tetragonal: $a = 8.93_4$Å; $c = 4.39_4$Å; $c/a = 0.49$.

## X-ray Studies on the Ni Coating

Investigations on the structure of the Ni deposit were carried out by Debye-Scherrer photographs of surface scrapings, Geiger counter tracings of surface reflections of the platings, transmission photographs of stripped films, and low-angle-scattering photographs of ground chips.

The Ni coatings showed the structure of an amorphous solid substance with "liquid-like" disorder of the atoms. Different base materials (such as Al, brass, steel, and Bakelite) and different pretreatments of Al base plates had no appreciable influence on the structure of the platings. The deposition of different thicknesses (1–10 mils) on these base materials had no influence on the amorphous structure of the coating.

The unique character of this physical state justifies a short discussion of amorphous solids and the experimental evidence for describing chemically reduced Ni plating as a liquid-like amorphous solid. The term "amorphous" is often used to describe structural forms for which more specific terms can now be given. In some deposits and dehydration products, a chaotic state of aggregation can be detected (13), e.g., small molecular groups loosely bound together in a quite irregular way show a high percentage of free space. The diffracted x-ray intensity of this gas-type, chaotic state extends continuously from the direct beam as in the case of diffraction of gases. The intensity of the scattered radiation in the vicinity of the central beam depends on the difference in scattering power or electron density between the two phases of the porous system. Other examples which show gas-type scattering are amorphous $SiO_2$, amorphous $Al_2O_3$, and highly dispersed carbon black (14).

With colloidal crystallites, the somewhat broadened central beam and the broadened diffraction lines are separated by distinct minima in the intensity of the scattered radiation. When the amorphous or crystallized particles are squeezed close together, the interstices are small compared with the particle size; the resultant intensity of the low-angle scattering is considerably decreased. All dense systems produce a weak, low-angle scattering, and this phenomenon can be used for analysis of the internal structure of the amorphous Ni.

A low-angle scattering x-ray photograph of ground chemically reduced Ni showed the very small scattering effect of a dense substance. This was probably not caused by pores between the amorphous aggregates but by the microlayer structure shown in the section on metallography and representing pseudo variations in P content.

In ordinary liquids, a clear intensity minimum separates the direct beam which is not broadened from the first diffraction band, i.e., the liquid halo. The x-ray patterns are characterized by a few wide bands, generally less than three (15). Distances which frequently occur between the atoms or molecules of the amorphous solid correspond to each halo on the diffraction pattern.

The x-ray powder patterns of chemically reduced Ni and the Geiger counter tracings of plated surfaces showed only one diffuse ring with a "*d*" spacing of 2.01Å. The occurrence of only one ring together with the extremely

small low-angle scattering characterize chemically reduced Ni deposits as liquid-like, dense, amorphous solids.

In the x-ray diagrams of liquids and liquid-like substances, the position of the peak intensity of the first halo corresponds approximately to the first strong line of the crystallized modification of the same substance. Closer investigation of the peaks of the x-ray patterns have shown, however, that in some cases the peaks do not coincide with the position of the strongest reflection of the crystallized compound. X-ray diagrams of vitreous silica, amorphous Se (obtained by quenching from a melt), and amorphous explosive Sb are examples of liquid-like amorphous solids with shifts in the positions of the halo (14, 16).

A visual inspection of the x-ray diagrams of amorphous and crystallized (heat treated at 430°C) Ni seemed to indicate that a similar shift of the position of the halo occurred with amorphous Ni. The sharp line of (111) reflections from crystalline Ni lay on the inner side of the halo. Because of the breadth of the halo and its diffuseness, a quantitative estimate of the shift was difficult.

Ring or line broadening could also have been caused by a very small crystalline particle size, but the broadening would have been symmetrical about the sharp line position. Furthermore, use of an approximate estimate of the halo breadth and the Scherrer formula for line broadening yielded the ridiculous answer of a mean particle size of a few atomic distance dimension. Electron diffraction patterns of 15 different chemically reduced Ni deposits plated under a wide variety of different conditions and in different thicknesses confirmed the amorphous character of at least the surface layers.

The density of amorphous Ni was determined in a pycnometer at 20°C and found to be $D_{20°} = 7.85$ g/cc.

The powder pattern of amorphous Ni heated in N for 1½ hr at 430°C showed a sharp line sequence of two structures. The Ni lines were easily distinguished. The remaining lines indexed provisionally on a tetragonal lattice of parameters $a = 9.01$Å and $c = 4.42$Å which is reasonably similar to the structure of $Ni_3P$ proposed by Nowotny and Henglein (2).

## A Metallographic Study of Chemically Reduced Ni

*Preparation of specimens for optical metallography.*—The first important phase of preparation was cutting and mounting specimens. The as-deposited coating was brittle, and simple cutting of a plated specimen with a hack saw tended to crack and flake off the deposit. It was convenient to electroplate the specimen with a heavy deposit of Ni to provide some support for the coating. The choice of Ni as a backing material was based on mechanical properties and final etching characteristics. Probably Cr would be too brittle to provide suitable support, and Cu would induce undesirable staining during etching. There was no difficulty in distinguishing the electroplated Ni from the chemically reduced Ni in polished and etched specimens.

Metallographic specimens are normally mounted in a thermosetting Bakelite under several thousand psi pressure. This method tended to promote formation of cracks in the plate, the so-called "dikes" observed by others

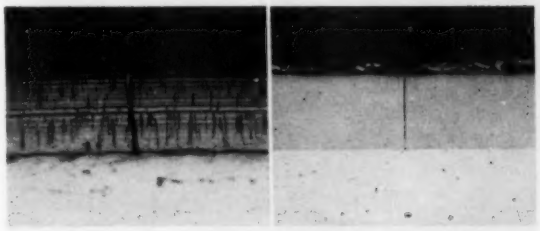

Fig. 2. (*Left*) Microstructure of 10 mil chemically reduced Ni on steel (etched). Fig. 3. (*Right*) Microstructure of 10 mil chemically reduced Ni on steel (unetched).

(Fig. 2 and 3). The etched structure revealed dark bands traversing the deposit from the substrate interface to the surface. On removal of the etch by repolishing, the dark band was more clearly resolved as a true crack.

It was possible to avoid the occurrence of cracks (which are artifacts) by mounting specimens in a room-temperature-setting compound, Epon, manufactured by the Shell Oil Company. This medium was mixed prior to casting with 8–10% by weight of triethylene tetramine which acts as a polymerizer. During curing the temperature remained below 50°C and no pressure was applied. The specimen was placed inside a polyethylene ring, approximately ½ in. high, 1 in. OD, and $\frac{1}{16}$ in. thick, which rested on a thin sheet of polyethylene film. The mixed resin was poured into the mold thus formed and allowed to solidify. Mounts thus prepared were ready for polishing in 3 hr.

Specimens for microexamination were processed as follows: (*a*) rough grind on a belt sander to create a flat surface, (*b*) rough lap on a cast iron lapping wheel with oil-suspended Carborundum abrasive, (*c*) rough polish (kerosene suspension of diamond powder), and (*d*) fine polish (water suspension of Linde "B" sapphire powder).

Routine etching reagents recommended for Ni alloys were unsuitable for revealing the structure of as-deposited chemically reduced Ni. An electrolytic etch was developed in which an electrolyte of 10% chromic acid in water was used. A cell potential of 2 v applied for about 5 sec was usually sufficient. Both cast chemically reduced Ni and heat-treated metal reacted satisfactorily to the standard $FeCl_3$-HCl etchant used for Ni alloys.

*Analysis of the structure of chemically reduced* Ni *coatings by optical metallography.*—Most of the studies were conducted on 10 mil plates on steel panels. On occasion it was easier to reveal the detail of basic structures on lump specimens of tank deposits.

In the unetched condition, platings at 1000 magnification were completely sound and showed no porosity, channels, or other types of voids. The plate followed the fine contour of the substrate surface in amazing detail. A number of the photomicrographs show burrs and other asperities with re-entrant angles. In all instances, the Ni deposited so completely that there were no observable voids between plating and substrate.

Fig. 4 and 5 illustrate some of the essential structural characteristics of chemically reduced Ni coatings. The structures reveal a peculiar array of parallel or concentric

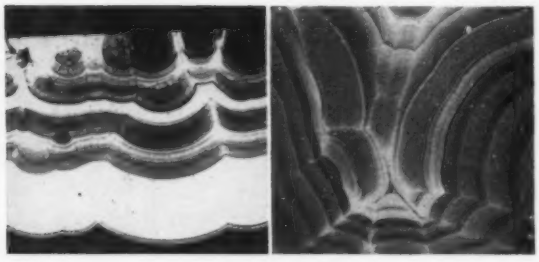

FIG. 4. (*Left*) Microstructure of tank deposited chemically reduced Ni in cross section. FIG. 5. (*Right*) Microstructure of tank deposited chemically reduced Ni in cross section.

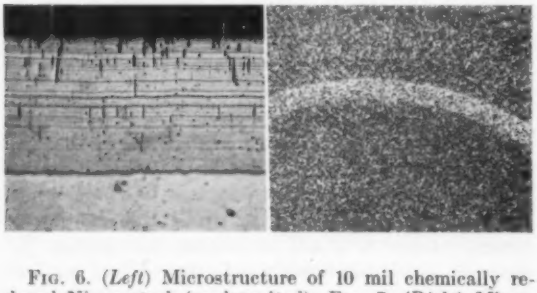

FIG. 6. (*Left*) Microstructure of 10 mil chemically reduced Ni on steel (as deposited). FIG. 7. (*Right*) Microstructure of a piece of tank deposited chemically reduced Ni after heat treatment at 700°C for 1 hr.

striations. These striations are characteristic of periodic variations of composition (presumably P) rather than alternate lamellae of different phases. Growth appears to originate at point centers or nuclei and develops at an equal rate in all directions, hence, the concentric circle pattern. When the two growth colonies meet, they generate a matching interface or fault. There is no evidence optically that the match at the fault is less than complete. If it were not true that x-ray diffraction patterns indicate an amorphous structure, these faults would come under the normal designation of grain boundaries. But since a grain boundary connotes an interface between two unique adjoining crystallographic orientations, the term cannot be properly used in this instance. It does appear, however, that the atomic disregistry at the fault is of the same degree as is thought to exist at a grain boundary, although this must be regarded only as reasonable conjecture.

On thin platings of the order of 10 mils and less, the population of surface nuclei is apparently so high that the spherical growth fronts join as a common "wave" front almost immediately, and the resultant structure shows the laminations as parallel (Fig. 6).

Evidence that the striations in the as-deposited chemically reduced Ni reflect variations in P content may be observed in microstructures of heat-treated deposits. By heat treatment the metastable as-deposited state reverts to the equilibrium phase mixture of Ni solid solution (containing very little P) and the intermetallic compound $Ni_3P$. The population of $Ni_3P$ particles may be used as an indication of the original P content. Fig. 7 shows the appearance of one of the original striations after heat

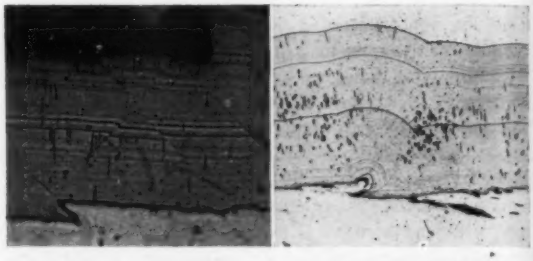

FIG. 8. (*Left*) Microstructure of 10 mil chemically reduced Ni on steel illustrating the effect of surface irregularities on the occurrence of growth faults in the deposit. FIG. 9. (*Right*) Microstructure of 10 mil chemically reduced Ni on steel illustrating the effect of surface irregularities on the occurrence of growth faults in the deposit.

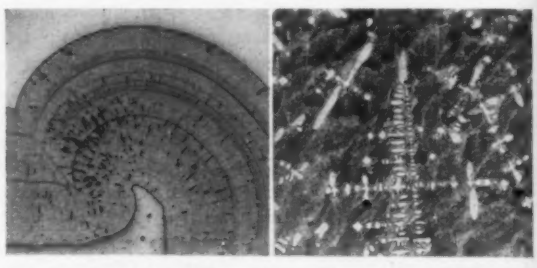

FIG. 10. (*Left*) Microstructure of 10 mil chemically reduced Ni on steel illustrating the growth of chemically reduced Ni around the burr of a sheared edge. FIG. 11. (*Right*) Structure of as-cast chemically reduced Ni—primary dendrites of Ni in a eutectic of Ni and $Ni_3P$.

treatment, and it can be seen that the number of $Ni_3P$ particles within the striation is less than on either side of it.

All the as-deposited coatings (Fig. 4 and 6) showed a series of secondary striations radiating from individual nucleus points or the surface. These secondary striations were discontinuous in pattern, and appeared only on etching. Therefore, they reflected some variation in chemical content. There was no vestige of them after heat treatment. Their nature could not be deduced from studies so far pursued.

Three microstructures are presented to illustrate the influence of surface imperfections on the structure of deposits on steel panels. Fig. 8 and 9 show the occurrence of burrs left on the steel by machining. In each instance growth faults originate from the surface irregularities. A particularly detailed picture of structures and growth faulting is illustrated in Fig. 10 at a sheared edge of a steel panel.

Fig. 8 is particularly important to the general theory of the deposition process. In the first set of parallel striations in the deposit, the displacement in adjoining growth areas is the same as the original displacement of the two surface levels on the steel. This indicates that growth rates are identical everywhere in the immediate vicinity, and that modifications in the reaction kinetics which develop different P content deposits occur at the same time over the surface, irrespective of their projection into the solution.

### Transformation Characteristics of Chemically Deposited Ni

*Nature of transformations.*—Since it was concluded that the as-deposited Ni may be interpreted as a liquid-like structure in which the primary alloy element, P, is randomly distributed on an atomic scale, the structure is metastable, both with respect to crystallinity and with respect to an equilibrium phase mixture of Ni solid solution and a Ni-P intermetallic phase, $Ni_3P$.

The ultimate equilibrium state was easily developed by melting a lump of chemically reduced Ni originally deposited on tank walls. The microstructure illustrated in Fig. 11 shows primary dendrites of Ni solid solution and a fine but resolvable eutectic of Ni and an intermetallic compound. The actual configuration seen in Fig. 11 is characteristic of the solidification process, but the products of crystallization are identical to what must ultimately derive from heat treatment of chemically reduced Ni below its melting point. X-ray diffraction powder patterns of the cast material gave a sharp pattern from which lines of the Ni structure could be easily distinguished from those of the intermetallic compound.

*Metallography of heat treated chemically reduced* Ni.—Fig. 12 and 13 illustrate structural configurations developed at two temperatures of heat treatment. In each case the transformation proceeded to equilibrium as revealed by x-ray diffraction patterns. The transformation to equilibrium produced a dispersion of $Ni_3P$ in a Ni matrix. Clearly, the size of the $Ni_3P$ particles was temperature dependent, i.e., the lower the heat treatment temperature, the finer the dispersion. The structure of a specimen annealed for 1 hr at 400°C was so fine that the particles cannot be individually resolved.

Generally, it may be inferred from such a sequence of microstructures that the finer the dispersion, the harder the structure. This is shown by hardness tests which show a progressive decline in the hardnesses of structures annealed at 400°, 500°, 600°, 700°, and 800°C. Hardnesses for these temperatures (1 hr anneal) were 1195, 980, 739, 665, and 544 VHN, respectively. Furthermore, it may be inferred that if some ductility can be induced in this material, it will be by annealing at 800°C or as close to the melting point as possible.

*Kinetics of transformation.*—It was found by experiment that hardness can serve as a tool for following time dependence of the state of transformation. Coupons were cut from a steel panel plated with a 10 mil deposit of chemically reduced Ni. The coupons were then annealed for specific times at 200°, 300°, or 400°C. Vickers hardness measurements were taken of the heat-treated Ni in the plane of cross section after cold mounting and polishing. A microhardness tester is mandatory for this type of work. In this instance, a Leitz instrument with a 100 g load was used. Reported hardnesses are averages of 5–10 measurements.

Trends of hardness vs. time for three temperatures are shown in Fig. 14. At 400°C a hardness peak is reached in about 10 min. Actually, in x-ray diffraction patterns the amorphous halo disappears after only 1 min at temperature and only the sharp lines of Ni and $Ni_3P$ appear. There is a question then of why hardness continues to

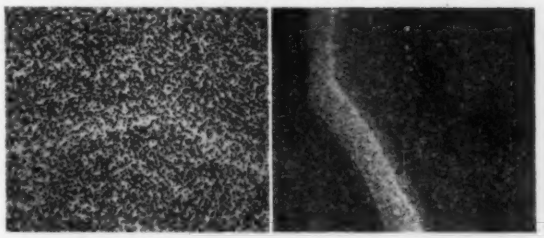

Fig. 12. (*Left*) Structure of chemically reduced Ni after heat treatment for 1 hr at 800°; dispersions of $Ni_3P$ in a matrix of Ni. Fig. 13. (*Right*) Structure of chemically reduced Ni after heat treatment for 1 hr at 600°C; dispersions of $Ni_3P$ in a matrix of Ni.

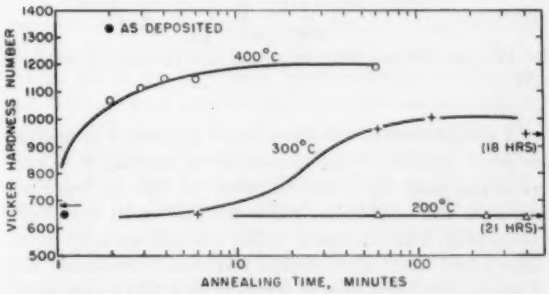


Fig. 14. Hardness of chemically reduced Ni vs. time and temperature of heat treatment.

increase after 1 min. It may be that transformation proceeds by two successive processes: a reversion from undercooled liquid solution to a supersaturated crystalline solution, then a rejection of $Ni_3P$ from the crystalline supersaturated solid solution. There are differences in relative intensities of lines and in the occurrence of certain lines in patterns taken after 1 min and after 60 min of heat treatment. Whatever the processes involved, the times are so brief that control short of complete transformation would be impractical.

At 200°C, even after 21 hr of heat treatment, there was no measurable change in hardness. X-ray patterns also showed the same amorphous halo observed in the as-deposited state. Accordingly, it may be concluded that no transformations occur at 200°C, at least none within 21 hr.

The 300°C anneal, as expected, followed a trend of slow transformation. Hardness continuously increased over a 2-hr period. As at 400°C, the amorphous structure, although it persisted for at least 5 min at temperature, disappeared long before the hardness reached a peak value.

*Thermal evolution during heat treatment of chemically reduced* Ni.—One of the main questions regarding the nature of the as-deposited metal is whether the structure is that of an undercooled liquid or of a submicroscopically fine-grained supersaturated solid solution. If the particle size of crystalline aggregates is small enough, the line broadening conceivably could approach the magnitude customarily found with undercooled liquids. One of the methods for distinguishing between these alternatives is through a study of x-ray low-angle-scattering and x-ray diffraction characteristics which are discussed in another section of this paper.

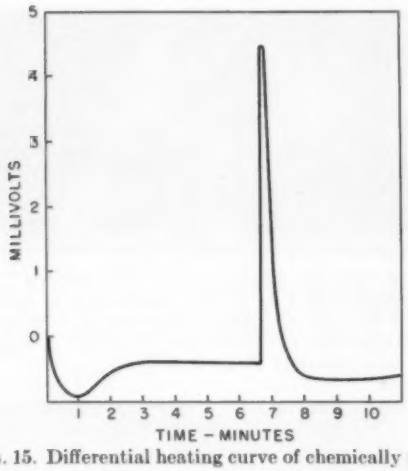


FIG. 15. Differential heating curve of chemically reduced Ni.

A second method which can give a qualitative indication is some measure of the magnitude of thermal evolution accompanying the transformation of the as-deposited metal to the equilibrium phase mixture of Ni and $Ni_3P$. Invariably, latent heats of fusion are substantially larger than latent heats of crystalline state transformations. For instance, the latent heat of fusion of Fe is 3700 cal/g-mole, whereas the heat of transition from $\alpha \rightarrow \gamma$ Fe is only 210 cal/g-mole; under adiabatic conditions these would correspond to temperature rises of 330° and 21°C, respectively. A survey of available data on latent heats of transformation indicates that they are all less than 1000 cal/g-atom and usually much less. Such thermal evolutions should then incur ideal temperature rises of less than 100°C, but since an ideal adiabatic system is very difficult to attain, the temperature rises should actually be considerably less.

A simple experiment was devised to study thermal evolution effects in chemically reduced Ni. Two pieces of Ni tank deposit in the form of plates about 0.020 in. thick and 1 $cm^2$ area were chipped to size. One piece was heat treated in advance so that no further transformations would occur. A fine wire chromel-alumel thermocouple was spot welded to each of the pieces and connected in opposition to a Speedomax high-speed recording potentiometer. Each of the pieces of chemically reduced Ni was set in a test tube for convenience of handling, and the assembly was immersed in a lead bath.

Since both pieces were heated at about the same rate, differential potential remained about zero. At 400°C, as recorded by an auxiliary thermocouple, there was a sharp rise in differential potential which lasted for about 1¼ min and then disappeared. A reproduction of this portion of the record is shown in Fig. 15. The burst of differential potential verified that the chemically reduced Ni liberated a substantial amount of heat on transformation to its equilibrium state. Furthermore, it is obvious that the transformation rate at 400°C is extremely rapid.

The maximum differential potential was 5 mv, which corresponds to a temperature rise during transformation of 122°C. Since the conditions of testing were far from adiabatic, this corresponded to a thermal evolution of considerably more than 1000 cal/g-mole. These results lend support to the hypothesis that as-deposited chemically reduced Ni is an undercooled liquid.

## Summary

The Ni deposit containing 7–10 w/o P produced by the catalytic Ni deposition process has been found to possess a dense, amorphous, liquid-like structure. It is probably the first occurrence of an amorphous metallic solid in massive form. The structure is unrelated to the nature of the substrate, manner of preparation, and thickness. The deposits were shown to conform, within microscopic resolution, exactly to the surface contour of the substrate. The deposit itself showed no porosity but in the etched state revealed striations in etching intensity and growth faults originating from asperities in the substrate surface. These striations in etching intensity were interpreted as banded variations in P content.

The as-deposited state of chemically reduced Ni is highly metastable and at 300°C or above reverts rapidly to the equilibrium condition of a phase mixture of crystalline Ni and crystalline $Ni_3P$. The dispersion of $Ni_3P$ in Ni can be used as a means for promoting and controlling hardness of heat treated chemically reduced Ni.

## Acknowledgments

This work represents part of a program sponsored by the General American Transportation Corporation at the Armour Research Foundation, and their permission to publish is gratefully acknowledged. Some of the x-ray diffraction studies were conducted by Miss Irene Corvin. Mr. E. Klimek was responsible for the metallography. Useful discussion was contributed by Dr. R. J. Spraul and Mr. W. J. Crehan of the sponsoring company.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1957 JOURNAL.

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# Electrochemical Properties of a Cation-Transfer Membrane

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ABSTRACT

The electrochemical behavior of a cation-transfer membrane with respect to cations of various charge was investigated. Measurements were made of capacity, water content, Donnan sorption, conductance, water transfer, and transport numbers. Results suggest that ionic mobilities are lower in the membrane than in free solution, indicating a high degree of association between the cations and the charge centers of the membrane.

Previous measurements of electrochemical properties of ion-exchange membranes have been confined almost exclusively to their behavior with univalent ions. In this paper comparative data are presented for a single cation-permeable membrane equilibrated with aqueous solutions of K, Ba, La, and $ThCl_4$, as representative of uni-, di-, tri-, and tetravalent cations. At a series of solution concentrations, measurements were made of the Donnan sorption equilibria, membrane conductance, cation transport numbers from membrane potentials, cation transport numbers from Hittorf-type measurements, and water transfer. The membrane[3] studied was a sulfonated, cross-linked, polystyrene-type, cation-exchange resin, cast as a homogeneous film, prepared as described in (1), and with properties as reported below. Experimental measurements, made at laboratory temperature, were not designed for a high order of accuracy, but to establish general membrane behavior. Results are discussed in terms of existing theories and possible structural concepts.

## Theoretical

A sheet of ion-exchange resin forms a permselective ion-transfer membrane, with fixed electrochemical properties determined by the solution with which it is equilibrated (2). In equilibrating solutions of high ionic strength, Donnan sorption of equilibrating electrolyte MX into the resin phase MR increases the concentration of M but also introduces an equivalent quantity of $X$ into the resin phase (3). Thus the cation transport number in the membrane decreases (from unity at low ionic strength of equilibrating electrolyte, when the only mobile species is M) to a value determined by the concentrations and mobilities of the sorbed species, and the membrane conductivity rises from similar considerations (4).

*Donnan sorption.*—When an ion-exchange membrane is immersed in a salt solution, the structure is penetrated by both positive and negative ions of the salt until the position of thermodynamic equilibrium is obtained where the partial molal free energy of the salt is equal in the membrane and solution phases. Assuming the same standard state for the ions in the membrane as in solution, expression of this Donnan equilibrium for a salt such as KCl leads to the relation $\gamma_{\pm s}^2\,(K^+)_s\,(Cl^-)_s = \gamma_{\pm m}^2\,(K^+)_m\,(Cl^-)_m$ where $\gamma_\pm$ represents mean activity coefficients, the quantities in parentheses represent concentrations, and subscripts $s$ and $m$ refer to the solution phase and membrane phase, respectively. Little is known of activity coefficients of ions in the membrane phase, so this relation cannot be verified independently. As has been pointed out (3–6), Donnan sorption in ion-exchange resins is significant, but is not explained from classical theory without assuming enormous variations in activity coefficients in the resin phase at low concentrations of equilibrating electrolyte.

In this paper, observed Donnan sorptions in the range 0.1–1.0$N$ equilibrating solutions are reported and used in conjunction with transport numbers and conductance values to compute apparent ion mobilities.

*Membrane conductivity and ionic mobilities.*—The specific conductivity of a membrane ($L$) can be determined in an appropriate conductivity cell (7). From the conductivity and transport number measurements, individual ionic conductivities $L_M$ and $L_X$ and equivalent ionic conductivities $\lambda_M$ and $\lambda_X$ in the resin phase may be defined as: $L_M = LT_+$; $L_X = L(1 - T_+)$; $\lambda_M = 1000\,L_M/(M) = 1000L\,T_+/(A) + (R)$; $\lambda_X = 1000\,L_X/(X) = L(1 - T_+)/(A)$ where $L$ represents the conductivity of the membrane (mho/cm), $L_M$ cationic conductivity; $L_X$ anionic conductivity; $T_+$—true cation transport number; $\lambda_M$—cation equivalent conductivity; $\lambda_X$—anion equivalent conductivity; $(M)$—concentration of cations, millieq./wet resin; $(X)$—concentration of sorbed anions, millieq./wet g resin; $(A)$—concentration of sorbed ions, millieq./wet g resin; $(R)$—concentration of ionized exchange sites, millieq./wet g resin.

*Transport numbers and water transfer from Hittorf measurements.*—The true transport number ($T_+$) of a cation across the membrane and the accompanying water transfer can be determined in a Hittorf cell. In such a cell the electrical transfer of ions through a membrane is accompanied by a flow of water, and the high hydraulic resistance of the membrane enables the extent of this water transfer to be measured.

When current is passed through a chloride solution contained in a cell bounded by a membrane and an electrode reversible to chloride, the transport number is given

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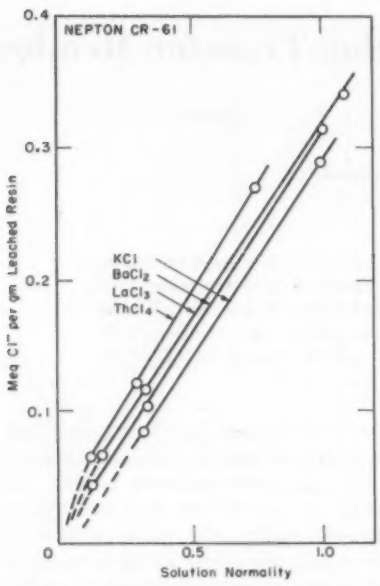


FIG. 1. Donnan sorption of salts in the membrane[2]

by $d(NV)d\mathbf{F} = NdV/d\mathbf{F} + VdN/d\mathbf{F}$ where $N$ and $V$ are the normality and volume (in liters) of the solution, and $\mathbf{F}$ represents the Faradays of electricity passed.

The electrical transfer of ions through a membrane is accompanied by water transfer, which can be expressed as $V^* = dV/d\mathbf{F}$ liters transferred per Faraday passed. It can be measured unambiguously in a Hittorf-type cell without a knowledge of whether the source of the transfer is endosmosis or ion hydration, or a combination of the two. Corrections must be made for the change in volume due to the electrode processes and volume of salt transferred. These corrections are small and have been calculated from published values of the partial molal volumes of the salts (8) and the densities of Ag and AgCl.

The transferred water, however, may carry with it salt from one electrode chamber to the other, and the concentration of this "water-transported" salt has a value $N'$ between zero and $N$. It contributes $N'dV/V$ to $dN$ so that the true transport number of $T_+$ is given by

$$T_+ = V(dN/d\mathbf{F} - N'dV/Vd\mathbf{F}) + NdV/d\mathbf{F}$$
$$= VdN/d\mathbf{F} + (N - N')dV/d\mathbf{F}$$

Since there is no means of determining $N'$, its value is set arbitrarily at zero, and the values of $T_+$ so obtained set an upper limit for the value of the transport number, the lower limit of which is set by $VdN/d\mathbf{F}$.

*Transport numbers from cell potentials* (9, 10).—Cation transport numbers across a membrane can also be determined from emf measurements. The emf developed between Ag-AgCl electrodes immersed in two chloride solutions of different concentration separated by a membrane is given by $E = t_+(RT/n\mathbf{F}) \ln [(m_{\pm 2}\gamma_{\pm})_2/(m_{\pm 2}\gamma_{\pm})_1]$ where $m_{\pm 2}$, $m_{\pm 1}$, $\gamma_{\pm 2}$, and $\gamma_{\pm 1}$ are the mean molarities and stoichiometric activity coefficients of the electrolytes, and $t_+$ is the apparent cation transport number in the membrane uncorrected for water transfer. This corresponds to $VdN/d\mathbf{F}$ in the expression above, and values from the two methods of measurements have been compared.

## EXPERIMENTAL

*Capacity, water content, and density.*—The membrane[3] as purchased was a sheet-form ion-exchange resin supported on a glass fiber backing. In the specimens employed in the present work (10 x 3 x 0.08 cm), the fiber constituted 24% by weight of the total membrane.

Water content was determined by drying at 110°C to constant weight. The water content of the backed material was 44% corresponding to 58% for the unbacked resin.

The capacity of the membranes was determined by converting a sample of known weight to the H form by equilibrating with 1$N$ HCl, followed by leaching with water and subsequent exchange with 1$N$ NaCl solution. The liberated H ion was titrated with standard alkali. The capacity (expressed as eq./1000 g water-equilibrated resin) was 0.87, corresponding to 1.15 for the unbacked wet resin. The capacity (expressed as eq./1000 g dry resin) was 2.75 on the unbacked dry resin.

The density of the membrane in the leached Na form was determined by measuring the dimensions of a rectangular specimen of known weight. The density (expressed as g/cc) was 1.27, corresponding to 1.09 for the unbacked resin.

*Donnan sorption.*—Data were obtained for the Donnan sorption of KCl, $BaCl_2$, $LaCl_3$, and $ThCl_4$ in the membrane.[3] Samples of the membrane of known weight were immersed in solutions of each salt at various concentrations. After equilibrium had been attained, the supernatant solution was withdrawn and analyzed; the membrane sample surface was dried, then leached with water until free of chloride. A chloride analysis of the leach water was made, from which the equilibrium concentration of chloride in the membrane and solution phases was determined. It is recognized that this technique yields only "leachable" chloride, i.e., sorbed chloride capable of desorbing into water. The experimental procedure allowed errors of ±5% in 1$N$ solutions, increasing to ±15% in 0.1$N$ solutions, in the data which are presented as Fig. 1.

*Membrane conductivity.*—A cell for determining the conductance of membrane strips has been described (7). Strips with dimensions 10 x 3 x 0.08 cm were equilibrated with salt solutions of various normalities, withdrawn from the solution, and surface-dried with fiber. Specific conductivities (mmho/cm) of these strips were then determined. Results are presented graphically in Fig. 2. The experimental procedure allowed probable errors of ±5% in conductivity values. Equivalent conductance values are based on the total volume of the leached membrane and are therefore relative values. The ambiguity of the term "solvent" in a solid phase containing 50% organics and 50% water prevents the use of a molal basis for conductance values.

*Transport numbers and water transfer from Hittorf measurements.*—Hittorf transport numbers were measured in a four-compartment cell consisting of a Ag disk, a membrane disk, a Ag disk, a membrane disk, and a Ag disk,

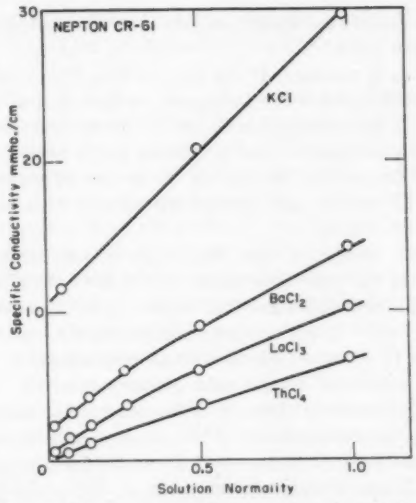


FIG. 2. Membrane conductance in salt solution

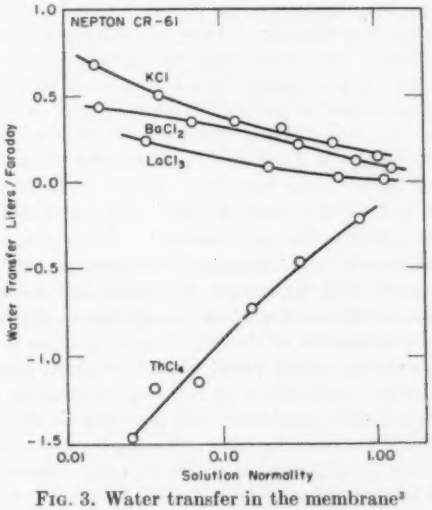


FIG. 3. Water transfer in the membrane[3]

separated from each other by plastic washers 1 cm thick with an OD of 10 cm and an ID of 5 cm. The centers of the washer disks formed the solution compartments, each of which was therefore bounded by a membrane and a Ag electrode. Each washer contained two tubes for filling and draining, and for connecting a graduated pipet on which volume changes were read. The Ag disks were given chloride coats sufficient to allow them to function as reversible electrodes for passage of up to 0.005 Faraday of electricity.

In an experimental run each compartment was filled initially with aliquots of a given solution and a voltage imposed across the two end Ag electrodes. With this arrangement it was possible to make quadruplicate determinations of concentration changes and volume changes simultaneously. Current was passed for a time sufficient to cause a concentration change of about 20%. Measurements were made of current, time, initial and final solution normality, and initial and final solution volume. From the

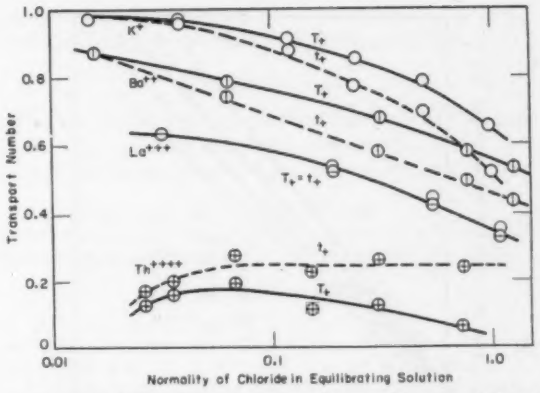


FIG. 4. Hittorf transport numbers with and without water correction.

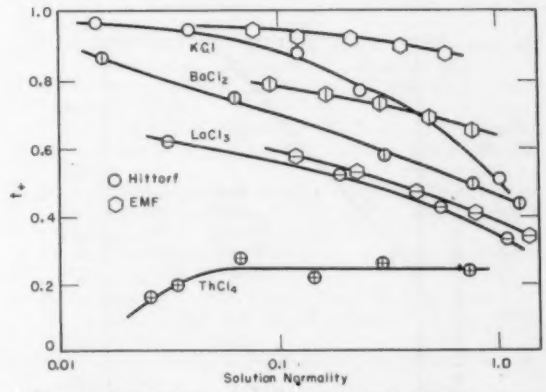


FIG. 5. Comparison of Hittorf and emf transport numbers.

data, the values of water transport (Fig. 3) and transport number (Fig. 4) were computed, corrections being made for the volumes of transported salt and the changes in volume at the electrodes. Probable errors in $V^*$ are about 3%, and in the transport numbers about 0.03.

*Transport numbers from cell potentials.*—In the determination of transport numbers from cell potentials, solutions were passed through two compartments of a Lucite cell separated by a membrane. In each experiment the salt concentration of the solution in one compartment was approximately twice the concentration of the other. The potential between Ag-AgCl electrodes immersed in the two solutions was measured on a potentiometer. From the observed potential, the concentrations, and activity coefficients, an apparent transport number was computed. The equilibrating solution concentration was taken as the geometrical mean of the two concentrations. Experimental techniques and uncertainties in activity coefficients result in a probable error of $\pm 0.03$ in the transport number values. Potentials in the $ThCl_4$ system were erratic and not reproducible, and transport numbers from emf measurements were not computed or reported for this ion. Transport numbers, $t_+$ (uncorrected for water transfer), as determined by emf and Hittorf methods, are compared in Fig. 5.

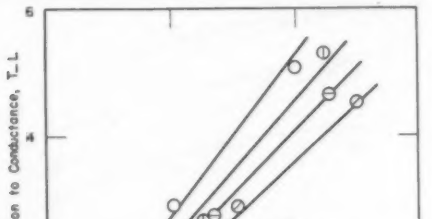


FIG. 6. Chloride contribution to conductance

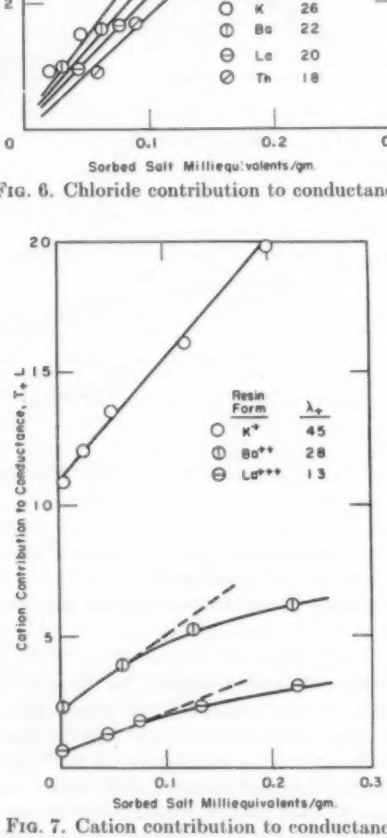


FIG. 7. Cation contribution to conductance

## DISCUSSION

*Donnan sorption.*—Fig. 1 shows an almost linear relationship between chloride concentration in the resin and chloride concentration in the equilibrating solution. This indicates that the exchange centers within the membrane are much less effective in excluding equilibrating electrolyte than would be predicted from capacity values. This discrepancy has been found to some degree in other ion-exchange work (3-6).

One possible explanation is that the cations are associated to a large extent with the exchange sites and thus are not effective in screening. An alternative description of the same physical situation is that, in the molecular pores of the membranes, the exchange cations are not distributed uniformly but are relatively concentrated at the walls of the pores and therefore ineffective in screening the center of these pores. The assumption of such association and estimates as to its extent based on observed conductivities are made below.

*Transport number.*—It can be seen from Fig. 5 that the agreement between the transport numbers, $t_+$, as determined by emf measurements and by Hittorf cell measurements, is not good in the K system, but is better in the Ba and La systems. Because of erratic emf measurements in the Th system, only Hittorf cell measurements are reported for this ion.

Trends discernible from Fig. 5 are of considerable interest. At the same concentration of sorbed chloride ion, the membrane shows greatest selectivity in the univalent system, while in the quadrivalent system the membrane appears to be anion selective at all concentrations. This view is supported by the water transfer data but cannot be finally confirmed because of the absence of transport number measurements for $ThCl_4$ in free solution. Some published work (11), however, shows that a major fraction of Th in chloride solution exists as $Th^{+4}$ and $ThCl^{+3}$, indicating anion transport numbers in free solution much lower than the value of 0.9 found in the membrane.

A possible explanation for the lower selectivity of the membrane to multivalent cations is that there is increased association of the cations with the charge centers of the membrane. If it is assumed that the exchange sites in the membrane cannot be deformed to allow association of more than one site with a cation, then the existence of positively charged centers in the membrane is possible. This would account for the lower transport numbers for multivalent cations and for the water transfer data and membrane conductance data discussed below.

*Water transfer.*—The passage of ions across a membrane is accompanied by the transfer of water, either as water of hydration of the transferred ions, as electro-osmotic water, or as a combination of the two. It is difficult to picture any experiments which would distinguish unambiguously the relative contributions of the two phenomena. In a cation-permeable membrane both processes would transfer water in the same direction as the ion transfer, and the magnitude of hydration of an ion crossing a membrane cannot be assumed to be that of the same ion in free solution. As seen from Fig. 3, water transfer values decrease with increasing concentration of sorbed salt and with increasing valence. They become highly negative in the Th system, offering some indication of the anionic character of the membrane in this form.

*Conductance data.*—Fig. 2 shows that the mobilities of the cations in the leached membranes differ much more markedly relative to each other than in free solution. This is in agreement with work of Boyd and Soldano (12) who found a similar strong dependence of self-diffusion coefficients on the ionic charge of the exchange ion.

*Ionic mobilities.*—It is possible to combine the experimental data on conductance, Donnan sorption, and transport numbers to calculate the relative mobilities of the various ionic species in the membrane. This has been done for the $K^+$, $Ba^{++}$, and $La^{+++}$ systems, the concentration units being expressed as millieq/g leached resin in the salt form under consideration.

The contribution of cations, including both exchange cations and Donnan-sorbed cations, to the membrane con-

ductance $L$ is given by $LT_+$, and the contribution of anions, which are present solely due to Donnan sorption, is given by $L(1 - T_+)$.

If $LT_+$ and $L(1 - T_+)$ are plotted as a function of Donnan sorption, it is found that the anion contribution is proportional to Donnan sorption. The computation of a nominal equivalent anionic conductance can be made from the ratio $LT_+$ to concentration. In Fig. 6 the equivalent conductance of the sorbed chloride varies from 18–26, depending on the exchange cation. This very small variation is striking in view of the large conductance variation in the leached resins in different ionic form. The equivalent conductance compares with a value of about 60 in aqueous NaCl of the same concentration.

The cation contribution is given by $LT_+$ (Fig. 7). Here the conductance is not zero at zero Donnan sorption because of the conductance due to exchange cations present.

There are two bases on which equivalent cationic conductances can be calculated. One estimate can be made by taking the increase in conductance as Donnan-sorbed salt concentrations increase, and represents the equivalent cationic conductance of the nonexchange cations. These estimates, from Fig. 7, indicate values of 45, 28, and 13 for $K^+$, $Ba^{++}$, and $La^{+++}$, respectively, and are not radically different from aqueous values. The other basis is to take the ratio of leached membrane conductance to exchange site concentration, which represents an equivalent cationic conductance of the exchange cations. These estimates, from Fig. 7, indicate values of 12.5, 2.7, and 0.7. In other words, the apparent mobilities of the exchange ions are much lower than those of the nonexchange ions. As pointed out by previous workers (4, 13), this can best be explained by assuming only partial dissociation of the resin salt. On this assumption the degrees of dissociation are 28%, 9.6%, and 5.4% for the salts KR, $BaR_2$, and $LaR_3$.

ACKNOWLEDGMENT

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# Kinetics of Metal Deposition

## Polarography Using Stationary Microelectrodes

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ABSTRACT

Current-voltage curves arising from metal deposition were determined using a variety of stationary microelectrodes, mostly vertical wires, and the concentration polarization approximated that expected from convective diffusion. The Nernst diffusion equation is not valid, and current densities $I$, in amp/cm², for systems containing excess inert electrolyte are given by the equation:

$$I = 1.4nFD^{0.5}(C - C_c)^{1.2}\left(\frac{1}{2r} + \frac{1}{\delta}\right)$$

This can be used to calculate limiting current densities during alloy formation and to characterize deposition processes as reversible or irreversible. Graphical methods can be used to determine transfer coefficients and rate constants, for a markedly irreversible process

The kinetics of diffusion to and reduction at a dropping mercury electrode has been studied extensively by means of current-voltage curves, but comparatively little work of a similar nature has been reported for metal deposition on solid microelectrodes. This is true despite the fact that such a technique could provide a simple method for evaluating rate constants and transfer coefficients of irreversible processes if the purely transport behavior could be adequately represented mathematically.

Following Wilson and Youtz (1), Glasstone (2) suggested that the simple Nernst theory of diffusion could be used to predict maximum current densities in plating baths. This approach, although an oversimplification, does predict the kinetics of many heterogeneous transport-controlled reactions with reasonable precision (3).

By far the largest proportion of recent work with solid micro-electrodes has been undertaken using an electrode moving relative to the solution, and the direct proportionality of current and concentration of reducible species is fully established. Use of stationary electrodes has much to recommend it on the grounds of simplicity and ease of reproducibility of experimental conditions. The approach has been used by Laitinen and Kolthoff (4) who reported that diffusion currents with a stationary Pt wire electrode were represented to a fair approximation by a Nernst type equation. The resulting direct proportionality of current and concentration has found analytical applications (5–8).

However, Levich (9) and Agar (10) deduced from theoretical grounds that for vertical macro plate electrodes convective processes should operate and limiting current densities be proportional to concentration raised to a power of five-fourths. This has been confirmed theoretically and experimentally for macro systems (11–16).

Despite this work, micro wire electrodes have been tacitly assumed to be some sort of exception. In the present work, a Nernst type of relationship with these electrodes was not confirmed, and current densities were reproduced with much greater precision and ease than generally assumed possible. The behavior of these systems is quite close to that to be expected if convective diffusion were operative. The purpose of this work is to establish a general equation applicable to polarography with these electrodes and to demonstrate the applicability of the equation to a study of electrode kinetics.

### Experimental Procedure

*Chemicals and apparatus.*—Metal perchlorates were prepared by evaporating nitrate solutions with excess $HClO_4$, fuming off the bulk of the acid, and neutralizing the remainder with NaOH. $NaClO_4$ was recrystallized and stored over neutral chromatographic activated $Al_2O_3$, and other salts were of analytical reagent quality. The metal content of all stock solutions (0.1M) was checked by standard chemical procedures. The final solutions of metals and inert electrolyte were adjusted to a *p*H just below the hydroxide precipitation values to minimize possible errors from H ion reduction.

The cell used in most experiments is shown in Fig. 1. The electrode was placed in the center compartment of the cell and the sheath, [5], passed over the cell. On placing the assembly in a water bath, thermostatically controlled to about ±0.1°C, a water seal was formed, and on passing electrolytic H through tube [1] to deoxygenate the solution, the residual H was held in [5] and formed a protective layer against the ingress of atmospheric oxygen. The two salt bridges, [2], were built onto the center compartment and curved round to dip into two half-cells, [4], the bridge ends being closed by sintered glass discs, [3].

The electrodes were prepared from Pt wire polished with fine emery, rinsed with aqua regia and then distilled water,

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and finally annealed. The disc electrode was in the form of a small circle cut from Pt sheet and sealed flush with the end of glass tubing of equal external diameter. The disc was held in a vertical plane, only one face being exposed to the electrolyte. To prevent the formation of "trees" of deposited metal on the sharp edges of the cut ends of the wire electrodes, the ends were covered by a bead of fused glass. The apparent surface area of the electrodes was measured to better than 1–2% by means of a cathetometer.

Currents were measured with a Sargent No. 21 polarograph and potentials to better than 1 mv by a Rubicon potentiometer. The precision and linearity of the polarograph was checked at all sensitivity settings by measuring the voltage drop across reference standard resistors and was found always correct to better than 1%.

*Procedure.*—Saturated calomel half-cells were prepared by the method of Hills and Ives (17) and the salt bridges filled with saturated $NH_4NO_3$. The center compartment was flushed and filled with the solution under study and the electrode inserted into the cell with the whole assembly in a constant temperature bath. H was passed for at least 30 min to remove dissolved oxygen. One half-cell was made the working anode and attached to the polarograph. The other half-cell was connected to the potentiometer and used to measure the potential of the microelectrode, giving values substantially free from $iR$ drop and liquid junction errors.

To prevent roughening and tree formation resulting from prolonged plating, the electrodes were stripped of metal between each reading. This was accomplished by lowering the applied potential to about 0.2 v more positive than the deposition potential of the metal (too great a positive potential sometimes led to electrode poisoning) and turning on a stream of H bubbles to stir the electrolyte. The stripping process, as judged by a negative current returning to a zero value, took only a few minutes. The only exception to this process was observed with the most dilute solutions or at very low potentials, when plating was so slow that several minutes were required to cover the electrode with deposit.

The blank currents from the base electrolyte, when determined without added metal ions, were negligible, provided that deoxygenation was adequate. However, in the presence of metal ions, in particular Tl, blank currents were sometimes obtained at voltages too low for metal deposition. The cause of this remains obscure, but what may be a similar type of behavior has previously been noted (18). If the electrodes were alternately plated and stripped several times these blank currents were nearly always entirely eliminated. Temperature control to within a few tenths of a degree was adequate, and current values did not seem to be unduly affected by normal laboratory vibrations, although precautions to minimize disturbances during measurements were observed. The sudden rise of current due to tree formation, particularly bad during alloy deposition, was quite characteristic, and, once recognized, could be eliminated as a source of error. However, without the blob of glass at the end of the wire electrodes, the onset of tree formation was often so rapid that reliable measurements could not be made. Some form of end covering was essential for accurate work at high current densities.

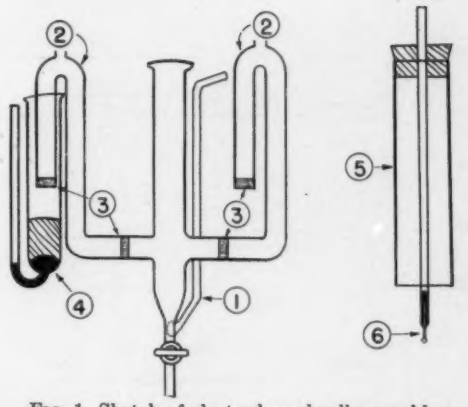


FIG. 1. Sketch of electrode and cell assembly

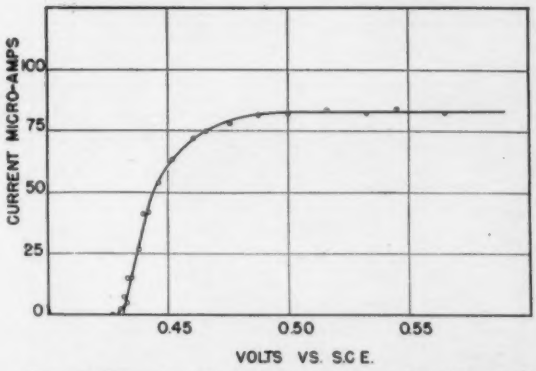


FIG. 2. Current-voltage curve for the reduction of 5.0 $\times 10^{-3}$ M $Pb^{2+}$ in 1M $NaClO_4$ at 25.0°C, using wire electrode of length 0.45 cm and radius 0.064 cm.

Diffusion coefficients, $D$, were determined polarographically. The best modification of the Ilkovic equation is still in doubt, but mainly as a result of the work of Wang (19) the Strehlow and von Stackelberg version (20) was used.

## RESULTS

The experimental data consisted essentially of current voltage curves such as that in Fig. 2. Limiting current densities were calculated from geometrical areas, and the mean value of at least four points was taken to determine a plateau such as that shown in Fig. 2. Reversible voltages were obtained by extrapolation to zero current.

The steady current value at each voltage was recorded as the mean of results taken every minute, after allowing 3 min for values to stabilize. As seen in Fig. 3, the initial high value for the current decreased during the first minute or so in a manner reminiscent of the behavior with linear diffusion, then rapidly became steadier, fluctuating slowly about a mean value which changed very little during a further 5 min or even longer. When eventually gross roughening or tree formations caused a marked rise in current the onset was nearly always obvious. In all cases fluctuations around a mean current never exceeded about ±5%,

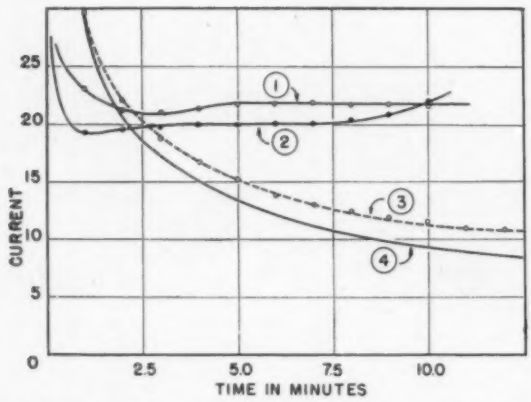


FIG. 3. Some representative current-time curves at constant potential. 1—Ferric → ferrous reduction; 2—$Pb^{2+}$ → lead metal deposition; 3—ferric → ferrous reduction at a sheltered horizontal disc electrode; 4—theoretical curve for linear diffusion.

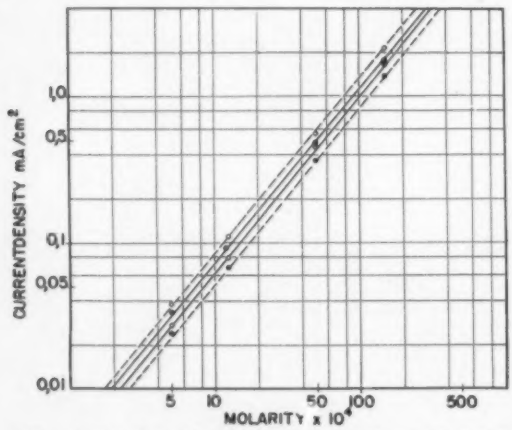


FIG. 4. Log $I_d$ vs. log $C$ plot. Open circles = Pb, blocked circles = Tl. Dotted lines = $2.45 \times 10^{-2}$ cm radius of wire. Full lines = $6.4 \times 10^{-2}$ cm radius wire.

TABLE I. *Exponent p under various conditions*

Electrode. $l$ = 0.423 cm $r$ = 0.0245 cm except where indicated.

| Ion | Concentration M × 10⁴ | Conditions of experiment | $I_d$ μamp/cm² | $p$ |
|---|---|---|---|---|
| $Pb^{2+}$ | 2.0 | 25°C 0.099M KCl | 12.2 | 1.19 |
| | 20.0 | | 189.5 | |
| $Pb^{2+}$ | 5.0 | 25°C 0.275M KCl | 35.4 | 1.21 |
| | 50.0 | | 575 | |
| $Ag^{+}$ | 15 | 25°C 0.5M $KNO_3$ | 92.4 | 1.21 |
| | 100 | | 915 | |
| $Fe^{3+}$ | 50 | 25°C 1.5M $NaClO_4$ | 91.0 | 1.23 |
| | 250 | | 660 | |
| $Pb^{2+}$ | 12.5 | 25°C No supporting | 120 | 1.23 |
| | 50.0 | electrolyte | 660 | |
| $Pb^{2+}$ | 12.5 | 4°C 1.0M $NaClO_4$ | 57.5 | 1.17 |
| | 50.0 | | 290 | |
| $Pb^{2+}$ | 12.5 | 25°C Disc electrode | 80.4 | 1.22 |
| | 50.0 | (0.427 cm diameter) 1.0M $NaClO_4$ | 438 | |
| $Tl^{+}$ | 12.5 | 25°C Disc electrode 1.0M | 63.1 | 1.19 |
| | 50.0 | $NaClO_4$ | 328 | |

and final limiting current plateau values could be obtained to better than ±2–3%.

Contrary to reports in the literature, limiting current density values were not proportional to the concentration of reducible ion but were proportional to this concentration raised to a power of near 1.2. This is seen in the logarithmic plot in Fig. 4 where an exponent of 1.20 ± 0.02 applies over a concentration range of $5.10^{-4}$M–$1.25 \times 10^{-2}$M for Tl and Pb in 1M perchlorate. Table I gives values for the exponent taken with a variety of reductions, including the redox system ferric-ferrous perchlorate, and the exponent is in the range 1.17–1.23 over a concentration range of about $2.10^{-4}$M–$2.5 \times 10^{-2}$M. The same behavior was found even when no inert electrolyte was present and when reduction took place at 4°C.

The current density for a wire electrode depended on the length and radius of the wire. For a given length it was proportional to a term $(1/2r + 1/\delta)$ where $r$ is the radius in cm of the wire and $\delta$ a parameter which (*see* below) should be a measure of the transport layer thickness. Fig. 5 shows data for the graphical evaluation of $\delta$ with the reduction of thallium and lead perchlorates at wire elecarodes, values being given in Tables II and III. The lines the drawn through the two means of four experiments with the wire electrodes of radius 0.064 and 0.025 cm, as these are the most precise values, but values for the other wire electrodes fall on the same line within reasonable experimental error. If $1/r$ is used for the small disc electrode values are again near the lines. A mean value of $3.3 \times 10^{-2}$ cm for $\delta$ was found.

Finally, current densities were found to be a function of the diffusion coefficients $D$ of the reducing salts in the base electrolyte employed. If the full current relationship is given by:

$$I_d = KnFD^qC^{1.2}(1/2r + 1/\delta) \qquad (I)$$

where $I_d$ is the limiting current density in amp/cm², $n$ the number of electrons involved in the reduction, F = Faraday, $D$ the diffusion coefficient in cm²/sec, and $C$ the concentration in moles/cm³. $K$ and $q$ can be evaluated graphically by plotting log $D$ against log $X$, where

$$X = I_d/nFC^{1.2}(1/2r + 1/\delta) \qquad (II)$$

This plot is shown in Fig. 6 from data given in Table IV. The method does not determine the value of $K$ and $q$ unambiguously, but 1.4 and 0.80, respectively, give the best line for a wide range of diffusion coefficients. Considering the approximations involved in assuming a constant value for $\delta$ and the exponent of $C$ with such a wide variety of reducing and inert electrolytes, the fit may be considered good. Eq. (IA) predicts

$$I_d = 1.4nFD^{0.8}C^{1.2}(1/2r + 1/\delta) \qquad (IA)$$

to about 5% the limiting current density to be expected with stationary wire microelectrodes of length 0.4–0.5 cm when used for solid metal deposition at 25°C.

## DISCUSSION

With moving micro wire electrodes, the thickness of the transport layer adjacent to the electrode may be assumed to be negligible in comparison with the radius of the wire

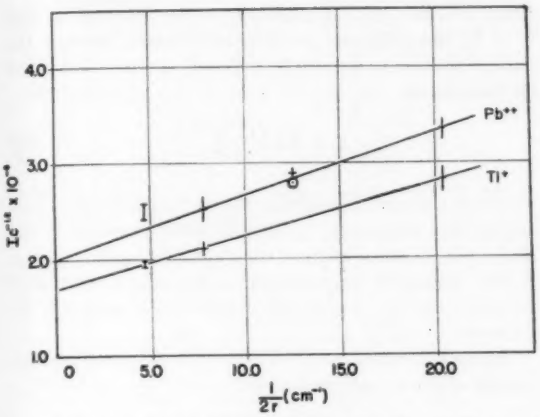


FIG. 5. Plot of $I_d \times C^{-1.2}$ against $1/2r$ for Pb and Tl plated onto various electrodes.

(say 0.5 cm), but with stationary electrodes this is not the case. A correction must be made to allow for the fact that when mass transfer takes place at a curved surface, the flux at the outer side of the transfer layer is greater than would be the case if transfer took place through a parallel sided segment. This is illustrated by Fig. 7*a*. Following the reasoning suggested by Strehlow (20), it can be assumed that the current density predicted for a plane electrode must be corrected by a factor greater than unity to allow for the increase of flux brought in by a curved layer. If the transfer layer is of definite fixed thickness with an approximately linear concentration gradient throughout, this factor should be roughly equal to the ratio of the volume of the actual layer to the volume of the layer adjacent to a plane electrode of the same area. In the case of a long cylindrical wire of radius $r$, the correction factor (Fig.7*b*) is $(\delta/2r + 1)$. Even for a disc electrode an appreciable correction may be necessary for transport around the elec-

TABLE II. *δ values. Thallous thallium in* $NaClO_4$ *at 25°C*

Graphical value for $\delta = 3.30 \times 10^{-2}$ cm

| Electrode length, cm | Radius, cm × $10^2$ | Concentration M × $10^4$ | Area, cm$^2$ | $I_d$ μamp/cm$^2$ | $I_d C^{-1.2} \times 10^{-5}$ | $\frac{1}{2r}$ | Calculated $\delta \times 10^2$ cm |
|---|---|---|---|---|---|---|---|
| Wire 0.45 | 6.4 | 5.0 | 0.184 | 23.9 | 2.17 | 7.8 | 3.2 |
| | | 12.5 | | 67.5 | 2.05 | | 3.45 |
| | | 50.0 | | 364 | 2.14 | | 3.3 |
| | | 150.0 | | 1390 | 2.16 | | 3.25 |
| | | | | | | | Mean 3.30 |
| Wire 0.423 | 2.45 | 5.0 | 0.065 | 32.9 | 2.98 | 20.4 | 3.05 |
| | | 12.5 | | 92.5 | 2.80 | | 3.4 |
| | | 50.0 | | 485 | 2.85 | | 3.3 |
| | | 150 | | 1740 | 2.70 | | 3.53 |
| | | | | | | | Mean 3.33 |
| | | | | | | $\left(\frac{1}{r}\right)$ | |
| Disc | 21.4 | 12.5 | 0.144 | 63.1 | 1.90 | 4.7 | 3.4 |
| | | 50.0 | | 328 | 1.95 | | 3.35 |

TABLE III. *δ values.* Pb *in 1M* $NaClO_4$ *at 25°C*

Graphical value for $\delta = 3.28 \times 10^{-2}$ cm

| Electrode length, cm | Radius, cm × $10^2$ | Concentration M × $10^4$ | Area, cm$^2$ | $I_d$ μamp/cm$^2$ | $I C^{-1.2} \times 10^{-5}$ | $\frac{1}{2r}$ | Calculated $\delta \times 10^2$ cm |
|---|---|---|---|---|---|---|---|
| Wire 0.45 | 6.4 | 5.0 | 0.184 | 27.2 | 2.50 | 7.8 | 3.35 |
| | | 12.5 | | 79.0 | 2.40 | | 3.5 |
| | | 50.0 | | 451 | 2.65 | | 3.1 |
| | | 150 | | 1640 | 2.55 | | 3.25 |
| | | | | | | | Mean 3.30 |
| Wire 0.33 | 4.0 | 50.0 | 0.083 | 531 | 3.12 | 12.5 | 2.9 |
| Wire 0.648 | 4.0 | 50.0 | 0.162 | 495 | 2.91 | 12.5 | 3.15 |
| Wire 0.423 | 2.45 | 5.0 | 0.065 | 38.0 | 3.45 | 20.4 | 3.15 |
| | | 12.5 | | 111 | 3.35 | | 3.35 |
| | | 50.0 | | 553 | 3.25 | | 3.5 |
| | | 150 | | 2155 | 3.33 | | 3.4 |
| | | | | | | | Mean 3.35 |
| | | | | | | $\left(\frac{1}{r}\right)$ | |
| Disc | 21.4 | 12.5 | 0.144 | 80.4 | 2.43 | 4.7 | 3.15 |
| | | 50.0 | | 438 | 2.58 | | 2.95 |

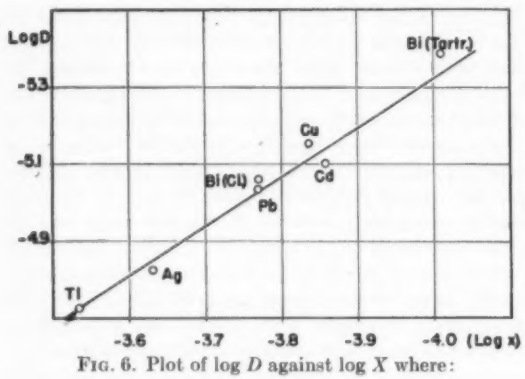


FIG. 6. Plot of log $D$ against log $X$ where:

$$X = \frac{I_d}{nFC^{1.2}\left(\frac{1}{2r} + \frac{1}{\delta}\right)}$$

TABLE IV. *Data for the evaluation of q and k in eq. (I)*

| Metal ion | Electrolyte | $D \times 10^5$ | $X \times 10^4$ |
|---|---|---|---|
| Tl | 1M $NaClO_4$ | 1.88 | 2.32 |
| Ag | 0.5M $KNO_3$ | 1.50 | 1.85 |
| Pb | 1M $NaClO_4$ | 0.92 | 1.35 |
| Bi | 1M KCl<br>0.1M HCl | 0.87 | 1.37 |
| Cd | 1M KCl | 0.80 | 1.10 |
| Cu | 1M $NaClO_4$ | 0.68 | 1.16 |
| Bi | 1M $HClO_4$ | 0.60 | 1.17 |
| Bi | 1M Tartaric acid | 0.41 | 0.775 |

$$X = \frac{I_d}{nFC^{1.2}\left(\frac{1}{2r} + \frac{1}{\delta}\right)}$$

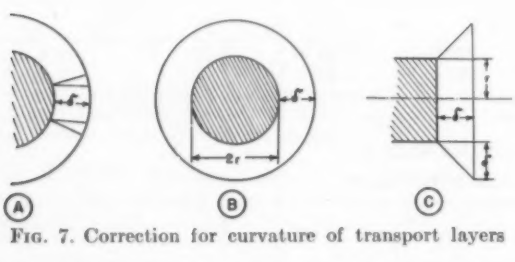


FIG. 7. Correction for curvature of transport layers

trode edge. Provided the radius of the disc exceeds about 0.1 cm, this correction factor (Fig. 7*c*) is roughly $(\delta/r + 1)$.

The hydrodynamic treatments of the problem of heat or mass transfer to a vertical plate (infinitely wide) all lead to an equation of the type:

$$(\text{Nusselt's number})^{\frac{1}{4}} = J(\text{Grashoff's number})^{\frac{1}{4}} \times (\text{Prandtl's number})^{\frac{1}{4}} \quad \text{(III)}$$

The factor $J$ is open to some doubt, but when using an average flux value over an electrode in aqueous electrolyte solutions, a value of 0.68 is probably best (13). This leads to the theoretical relationship that

$$\text{flux}_{\text{wire}} = \text{flux}_{\text{plane}} \times (\delta/2r + 1) \quad \text{(IV)}$$

$$\text{flux}_{\text{plane}} = \frac{D^{0.75} \times (C - C_e)^{1.25}}{Z} \quad \text{(V)}$$

where $D$ is the diffusion coefficient of the reducing ion and $C - C_e$ the difference in its concentration between the bulk of the solution and the electrode surface. $Z$ is given by the relation.

$$Z = 1.5\left(\frac{l\gamma}{g\alpha}\right)^{0.25} \quad \text{(VI)}$$

where $l$ is the vertical height of the electrode, $g$ is the acceleration due to gravity, $\gamma$ the kinematic viscosity of the electrolyte solution, and $\alpha$ a constant relating the relative density change between the bulk solution and solution at the electrode surface with the corresponding concentration gradient $(C - C_e)$.

Expressing flux in terms of current density and combining the above equations lead to:

$$I = \frac{\delta}{Z} nFD^{0.75}(C - C_e)^{1.25}\left(\frac{1}{2r} + \frac{1}{\delta}\right) \quad \text{(VII)}$$

Eq. (I) resembles the limiting form of this equation where $C_e \to 0$ and $K$ has the value $\delta/Z$. The experimentally determined exponents for $C$ and $D$ of 1.20 and 0.80 are at variance with theory over the range of conditions used. The trouble may be due to the assumption that density differences are exactly proportional to concentration differences (21). An approximate value for $Z$ can be calculated from eq. (VI). If $l$ is taken as 0.45 cm, $\gamma$ as $0.9 \times 10^{-2}$ cm²/sec, and $\alpha$ as 50 cm³/mole, $Z$ evaluates to about $2.5 \times 10^{-2}$ cm$^{\frac{1}{4}}$ sec$^{\frac{1}{4}}$ which gives a value for $K$ of around 1.3. As the current density is proportional to $l^{-0.25}$ the value of $K$ changes significantly if $l$ varies substantially from 0.45 cm. This was noted with the 0.33 mm electrode (Table III), and suitable correction was made when plotting data in Fig. 5 and 6. With wires exceeding about 0.75 cm in length, current values were found to be erratic and data were not precise enough to be useful.

The assumption that $\delta$ is sharply defined and constant under all conditions is not theoretically justified, but a mean value for a wire can be shown to change comparatively little under most conditions likely to be used in this type of polarography. Although the errors resulting from neglecting a correction for wire curvature may be serious, the errors in the correction itself are probably within the general experimental precision of the method. The value for $\delta$ measured optically by Ibl and co-workers for a small plate (15) were in agreement with the theoretical value given by Keulegan (12) and were near to $3.3 \times 10^{-2}$ cm at the current density values used in the present investigation.

As the exact value of $I$ is a critical function of the value of $K$ and the exponent of $D$, it is best to determine the constant $B$ equal to $\frac{\delta}{z} nFD^q(1/2r + 1/\delta)$ experimentally for any given reduction at a given wire electrode when the relation:

$$I = B(C - C_e)^{1.2} \quad \text{(VIII)}$$

should apply with considerable precision.

The behavior when two ions are transported and discharged simultaneously is shown in Fig. 8. Tl and Pb were chosen because they show complete mutual solubility in

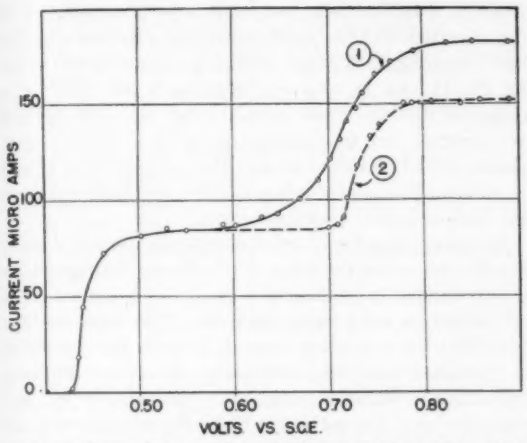


FIG. 8. Deposition of Pb and Tl separately and together with both ions at $5.0 \times 10^{-3}$ at 25.0°C in 1M $NaClO_4$. 1—Experimental; 2—curves to be expected if transport and deposition processes free from mutual interaction.

TABLE V. *Simultaneous diffusion of* Pb *and* Tl
1M $NaClO_4$ at 25°C
Limiting current densities

| Concentrations $\times 10^4$ M | | $I_{Pb} + I_{Tl}$ | $I_{total}$ found | $I_{total}$ calculated |
|---|---|---|---|---|
| Pb | Tl | | | |
| 50.0 | 50.0 | 815 | 990 | 990 |
| 50.0 | 12.5 | 517 | 595 | 595 |
| 12.5 | 50.0 | 444 | 520 | 540 |

the solid state and the diffusion coefficients of the ions differed by about 100%. The curve for Pb in the presence of Tl is identical with that for Pb alone. However, the subsequent deposition of Tl not only occurs at a lower potential, due to the free energy of solution of Tl in a Tl-Pb alloy assisting the reduction, but the limiting current for Tl appears to be enhanced some 40%. This enhancement is found for other ratios of Tl and Pb (Table V) and can be predicted with precision if it is assumed that the flux of ions depends on $C_T^{1.2}$, where $C_T$ is the total molarity of reducible ions, and a weighed mean of the $D^{0.8}$ values for each species. As the current equals the flux times the mean charge per particle, if $C_1$ and $C_2$ are the two concentrations of ions having charge, $n_1$ and $n_2$ and diffusion coefficients $D_1$ and $D_2$ respectively:

$$I_d(\text{Total}) = K\left(\frac{n_1C_1 + n_2C_2}{C_T}\right)\left(\frac{C_1D_1^{0.8} + C_2D_2^{0.8}}{C_T}\right) \cdot FC_T^{1.2}\left(\frac{1}{2r} + \frac{1}{\delta}\right) \quad \text{(IX)}$$

Values of $I_d$ obtained using this equation are given in the last column of Table V.

Eq. (VIII) can be used to test the reversibility of electrodeposition at a stationary electrode. Substituting for $C_e$ in the Nernst equation:

$$\text{Overvoltage} = \text{Constant} - \frac{2.3RT}{nF}\log\left(I_d^{0.83} - I^{0.83}\right) \quad \text{(X)}$$

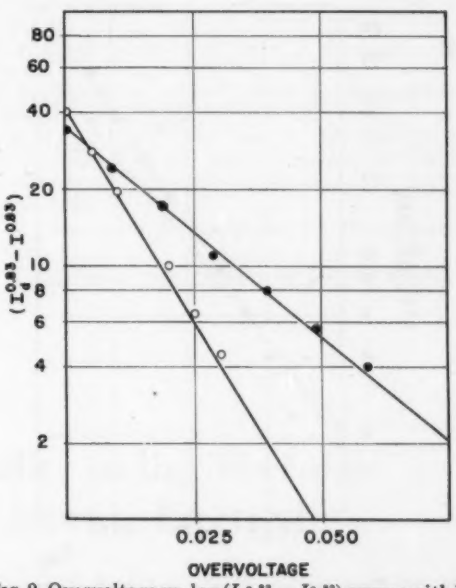


FIG. 9. Overvoltage vs $\log (I_d^{0.83} - I^{0.83})$ curves with lines drawn with theoretical slope of 0.0591 for Tl and 0.0296 for Pb.

and a plot of the data for Tl and Pb deposition from perchlorate gave points lying on lines of the theoretical slope as shown in Fig. 9. However, with most depositions a marked irreversibility is found, although eq. (VIII) can again be used. Values for a heterogeneous constant and transfer coefficient $\alpha$ can be obtained from polarograms, but the writing is tedious. At values $0.1/n$ v cathodic to the zero current potential, however, the rate of the back reaction (metal dissolution) can be neglected and the current can be written in the form:

$$i = nFA^1k_f^0\,C_e \exp\left(\frac{\alpha nF}{RT}E\right) \quad \text{(XI)}$$

where $E$ is on the H scale with Lewis-Randall sign convention, $C_e$ in moles/cc, and $A^1$ is the area of the reactive surface of the metal. This may well be considerably greater than the geometrical area affecting the transport process. If $k_f^e$ is defined as equal to $\beta k_f^0$, where $\beta = \dfrac{A^1}{A}$, then on substituting for $C_e$ from equation (VIII)

$$E = \frac{2.3RT}{\alpha nF}\log\left(\frac{I}{I_d^{0.83} - I^{0.83}}\right) - \frac{2.3RT}{\alpha nF} \cdot \log\left(\frac{nFk_f^e}{B^{0.83}}\right) \quad \text{(XII)}$$

where $I$ is in amp/cm² and $B^{0.83}$ is given by the relation

$$B^{0.83} = \frac{I_d^{0.83}}{C} \quad \text{(XIII)}$$

Plots of $E$ against $\log\left(\dfrac{i}{i_d^{0.83} - i^{0.83}}\right)$ are shown for Cu and Bi in Fig. 10. Where the back reaction can be neglected, points fall on a straight line the slope of which gives

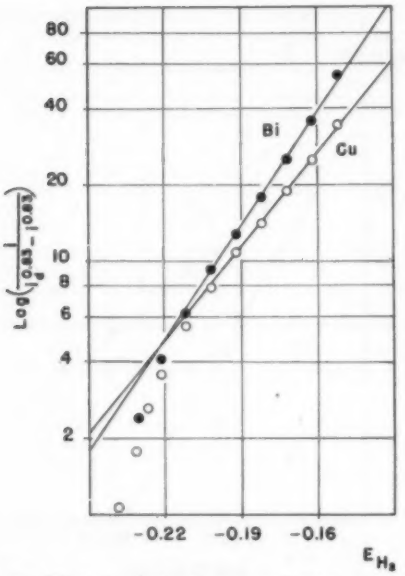


FIG. 10. Plots to determine $\alpha$ and $k_f^o$ for irreversible depositions. $4.0 \times 10^{-3}$M copper perchlorate in 1M $NaClO_4$ and $4.0 \times 10^{-3}$M bismuthyl perchlorate in 1M $HClO_4$.

where $E_r$ is the reversible potential in the given solution of concentration $C$. Data for $k^1$ and $I_0$ are also shown in Table VI with limiting values (assuming $\alpha$ equal to 0.5) given for Pb, Tl, and Ag where the reaction is too rapid to be measured directly. These data are only approximate and are reported here to illustrate the method. More precise studies with this technique and the comparison of $k^1$ and $I_0$ values obtained by this and other methods will form the basis of further communications.

The true value for $k_f^0$ and the exchange current density is unknown unless the value of $\beta$ is known, but ignorance of this number is common to a greater or lesser extent to all studies on solid metal electrodes. The apparent "reversibility" of a reaction depends on both the conditions of transport (diffusion, stationary convective diffusion, convection in stirred solution, etc.), the value for $k_f^0$, and the value for $\beta$. The statement that a deposition is or is not "reversible," therefore, cannot be generalized without reference to the technique employed. The present method relates, at least approximately, to normal electroplating practice.

ACKNOWLEDGMENTS

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TABLE VI. *Summary of kinetic data*

| Metal ion | Concentration $10^3$M | Base electrolyte | Zero current potential (H scale) | Alpha | $k_f^o$ cm/sec | $k^1$ cm/sec | $I_0$ amp/cm² |
|---|---|---|---|---|---|---|---|
| Thallous | 5.0 | 1M $NaClO_4$ | +0.47 | — | $>10^{-5}$ Reversible | >0.1 | >0.5 |
| Pb | 5.0 | 1M $NaClO_4$ | +0.19 | — | $>10^{-5}$ Reversible | $>10^{-2}$ | >0.01 |
| Ag | 4.0 | 0.5M $KNO_3$ | −0.63 | — | >1000 Reversible | $>2\ 10^{-2}$ | >0.01 |
| Bi | 5.0 | 1M KCl; 0.1M HCl | −0.12 | 0.55 | 1.5 | $7.10^{-4}$ | $10^{-3}$ |
| Cupric | 4.0 | 1M $NaClO_4$ | −0.25 | 0.35 | 0.65 | $7.10^{-4}$ | $5.5 \times 10^{-4}$ |
| Bi | 4.0 | 1M $HClO_4$ | −0.25 | 0.3 | 2 | $3.10^{-4}$ | $3.5 \times 10^{-4}$ |

$\alpha$, and the intercept enables $k_f^o$ to be calculated. A few values are shown in Table VI. The method is approximate, and apart from effects of impurities on the value of $\alpha$, the precision of the determination of $\alpha$ depends on the exact shape of the current-voltage curve near the top of the curve and the exact value of $I_d$. By taking sufficient points in this region, however, $\alpha$ values should be obtainable to about 10–15% and rough values for $k_f^o$ calculated. The method has the great advantage that these kinetic parameters are obtained under actual conditions of metal deposition when the entire surface is being refurnished with atoms several times a second, and many of the complications of using methods studying the reaction at the reversible potential with an a-c bridge (22) are avoided. A constancy of $\alpha$ with applied potential must be assumed but if this is the case:

$$I_0 = nFk^1C$$

where $I_0$ is the apparent exchange current density at concentration $C$ and $k^1$ is given by the expression:

$$k^1 = k_f^0\beta \exp\left(\frac{\alpha nFE_r}{RT}\right).$$

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# Preparation and Reproducibility of the Thermal-Electrolytic Silver-Silver Chloride Electrode

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ABSTRACT

Preparation of the thermal-electrolytic Ag-AgCl electrode for precision use is described. A reproducibility of the electrode of ±0.1 mv can be achieved readily by this procedure. Freshly prepared electrodes are evaluated relative to equilibrated Ag-AgCl electrodes selected as reference standards. With care, reference standards corresponding to an electrode in the ground energy state, and of constant potential (±0.005 mv) for periods of several months can be attained. It is suggested that the difference in the values of the standard potential of this electrode may be attributed in part to the limited reproducibility of these electrodes. The importance of the porosity, amount of AgCl, and color, relative to the attainment of stable electrodes that equilibrate rapidly, is considered.

The widespread use of Ag-AgCl electrodes as secondary reference electrodes of the second kind in emf measurements has been reviewed (1). The thermal-electrolytic electrode probably has been used more extensively than any other form in recent work. The procedure (2, 3) of preparation may be conveniently itemized as follows: (*a*) preparation of the electrode base, (*b*) precipitation and purification of $Ag_2O$, (*c*) application of the $Ag_2O$ paste, (*d*) thermal reduction of the oxide to Ag, (*e*) purification of the chloride to be used for anodizing, (*f*) chloridizing the Ag, and finally, (*g*) aging and bias potential tests prior to use. These points are covered here in sufficient detail to emphasize factors important in the preparation of reproducible and stable electrodes of precision quality. Concepts of the bias potential and aging tests are reexamined briefly as criteria in evaluating the quality of the Ag-AgCl electrode.

When identical kinds of electrodes are immersed in a solution so that the activity of the electrolyte to which the electrodes are reversible is the same at each electrode, there is no difference in potential, providing each electrode is in equilibrium with the solution in the ground energy state. In practice, differences in potential are often observed. The term "bias potential" is used here to denote this difference of potential.

The reproducibility of three types of Ag-AgCl electrodes was shown by Smith and Taylor (4) to be of the order of ±0.02 mv. It was stressed that intra-agreement in a set of electrodes at a given time is no criterion that their potential has come to equilibrium since an aging effect may be present. It was found that Ag-AgCl electrodes freshly chloridized were positive with respect to electrodes in equilibrium with a test solution. The origin of this was traced to concentration polarization. When the electrodes of the electrolytic and thermal-electrolytic types are chloridized, the solution within the pores of the AgCl coating becomes more dilute than the surrounding solution. The magnitude of the change in concentration can be estimated from the bias potential assuming the system approximates a concentration cell (4):

$$\text{Ag-AgCl} \mid \text{MCl}(C) \mid \text{MCl}(C - \delta) \mid \text{AgCl-Ag},$$

where $\delta$ is the effective decrease in the concentration of the electrolyte within the pores. The emf of this cell is given by

$$E = 2t_{M^+} RT/\mathbf{F} \ln C/(C - \delta)$$

(where $E$ is the emf, $t_{M^+}$ the transference number of the cation, $C$ and $C - \delta$ are the concentrations of the solutions about each electrode, respectively, and $R$, $T$, and $\mathbf{F}$ are the gas law constant, temperature, and Faraday, respectively) if the variation in ionic mobilities between the two concentrations is negligible, and if the activity ratio is equal to the concentration ratio. Substituting the bias potentials observed, typical concentration changes, $\delta$, are obtained for KCl and HCl as electrolytes:

| $E$ (mv) | 10 | 1 | 0.1 | 0.025 |
|---|---|---|---|---|
| $\delta$(KCl) | $0.33C$ | $0.04C$ | $0.004C$ | $0.001C$ |
| $\delta$(HCl) | $0.21C$ | $0.023C$ | $0.0023C$ | $0.0005C$ |

A freshly prepared electrode in the bias solution is thus positive relative to the aged reference electrode since $C$ is greater than $C - \delta$. The time required to attain equilibrium depends on the porosity, the concentration, and the stirring of the solution. In some cases it is as long as 20 days (4).

Even when care is exercised in preparation, equilibrated electrodes may still exhibit a constant, but finite, bias potential. Assuming that the aging process has proceeded to completion, as shown by a constant bias, a difference in energy states of the AgCl must exist. Thus, for two Ag-AgCl electrodes, A and B, in equilibrium with the common electrolyte, if A is negative in potential to B, then the cell reactions are:

| Electrode | Polarity | Reaction |
|---|---|---|
| A | Negative | Oxidation: $Ag + Cl^- \rightarrow AgCl_A + e$ |
| B | Positive | Reduction: $AgCl_B + e \rightarrow Ag + Cl^-$ |

Net cell reaction: $AgCl_B \rightarrow AgCl_A$.

Thus, the spontaneous reaction is the formation of more AgCl at electrode A at the expense of the silver chloride electrode B. Accordingly, the negative electrode, A, is in the lower energy state. The magnitude of energies corresponding to these bias potentials is as follows:

| $E$(mv) | $\Delta F$ (cal) |
|---|---|
| 1 | 23.07 |
| 0.1 | 2.31 |
| 0.02 | 0.46 |

Thus, a bias potential of 0.02 mv introduces an error of 0.46 cal in the free energy.

## Experimental

*Electrode base.*—The electrode base was a spiral (1 mm diameter) of 2–3 turns of 24–26 gauge Pt wire. This was sealed into a 4–6 mm diameter glass tube, or a ground glass extension joint, so as to leave the end of the wire protruding inside the tube for a mercury contact. Soft glass was preferable to Pyrex glass since it permits a neater, stronger seal. No observable differences in ultimate bias potentials were found to be attributable to the glass used. Soft glass was used in the present bias studies.

*Precipitation and purification of* $Ag_2O$.—$Ag_2O$ was precipitated from a vigorously stirred solution of $AgNO_3$ ($\frac{1}{4}$ equiv. of C.P. $AgNO_3$ in 750 ml of de-ionized water) by dropwise addition of $\frac{1}{2}$ equiv. NaOH in 100 ml of water. Vigorous stirring was continued until homogeneity and complete precipitation were ensured. An important precaution was thorough washing of the resulting precipitate to remove all water-soluble impurities. Bates (3) found that a number of washings was required to reduce the conductivity of the wash water to $3 \times 10^{-6}$ ohm$^{-1}$/cm. In the present work, with vigorous mechanical shaking, the conductivity was $4 \times 10^{-5}$ ohm$^{-1}$/cm for several washes. Calculations from solubility considerations predict $3 \times 10^{-5}$ ohm$^{-1}$/cm.

On washing to the above criterion (30 washes), $Ag_2O$ was recovered in a sintered glass filter. Subsequent use of this material as an aqueous paste necessitated only a superficial drying by a short continuation of the suction. Both the filter and the storage weighing bottle were cleaned in a standard fashion (hot chromic acid followed by repeated rinses with distilled water, and final cleaning with hot water) the filter by passing near-boiling water through it, and the bottle by boiling in water for $\frac{1}{2}$–1 hr.

*Application of* $Ag_2O$ *Paste.*—$Ag_2O$, when mixed with water, forms a paste such that it can be applied easily to the Pt spirals with a small spatula. With the inside of the spiral completely filled and the wire totally covered (except for a few mm between glass and spiral), a sphere of 3–4 mm diameter was obtained. Prior to application of the paste, the Pt spirals were cleaned by boiling briefly in concentrated $HNO_3$ followed by repeated flushings with distilled water and boiling in de-ionized water.

In the application of a second coat, a much thinner consistency was used, so that the paste almost yielded to gravity when held on a spatula or when suspended from the sphere of silver.

*Thermal reduction of* $Ag_2O$ *to* Ag.—Electrodes for thermal reduction were suspended in the central portion of the furnace well (Hoskins, type FD14) by means of a simple support fashioned from two parallel squares of heat-resistant asbestos board separated by 1.5 in. spacers. Rubber bands held the electrode in place in vertically coincidental holes. A centrally located hole admitted a thermocouple.

In order to preclude the possibility of "sputtering" by the rapid formation of steam, the electrodes were maintained in the furnace at just below 100°C for $\frac{1}{4}$–1 hr to permit superficial drying. The temperature was then raised at a uniform rate to 450°C. The latter temperature was held for $\frac{1}{4}$ hr further to complete the reduction to porous Ag. The electrodes were permitted to cool within the furnace to avoid thermal shock.

Reduction of the second coat of AgO proceeded in a completely analogous manner. The electrodes were finally stored in a desiccator for protection until required for the chloridizing.

*Purification of chloridizing electrolyte.*—The need for purification of the chloride for anodizing was clearly demonstrated (5). For example, the potential increased by 0.1–0.2 mv for each 0.01 mole % bromide in solution. Removal of trace impurities of bromide, therefore, is an important aspect in the purification of the electrolyte to be

TABLE I. *Description of thermal-electrolytic* Ag-AgCl *electrodes*

| Electrode set | K | A | B | C | D |
|---|---|---|---|---|---|
| No. of Ag coats | 2 | 1 | 2 | 1 | 2 |
| Wt. Ag (g) | 0.0702 | 0.1214 | 0.0822 | 0.1481 | 0.1087 |
| AgCl (%) | 10.5 | 5.5 | 8.2 | 4.5 | 16.2 |
| Current (ma) | 10 | 1 | 1 | 10 | 10 |
| Chloridized in | 0.05*N* KCl | 1*N* HCl | 1*N* HCl | 1*N* HCl | 1*N* HCl |
| Aged in | 0.05*N* KCl | 0.1*N* HCl | 0.1*N* HCl | 0.1*N* HCl | 0.1*N* HCl |
| Equilibrium (hr) | 10 | 8 | 4 | 20 | 6 |
| Surface area ($m^2/g$) | 0.3 | 3.4 | 0.3 | 3.4 | 0.3 |

used for chloridizing and subsequent potential measurements. In the present work, KCl was purified by the Pinching-Bates method (5).

Concentrated HCl for subsequent dilution was prepared by azeotropic distillation (6). HCl (C.P.), diluted with de-ionized water to the recommended density of 1.10 g/ml, was used as the starting material. The condenser and fittings were quartz. The final distillate was stored in a quartz flask.

*Chloridizing the* Ag.—The Ag electrode was chloridized by making it the anode in a simple U-tube cell. The electrode chambers were 8 cm long and 2 cm in diameter. The central portion was constricted to 1 cm while fashioning the U-bend. Pt spirals, similar to those used for the preparation of Ag electrodes, served as cathodes. A current of 10 ma was passed through an assembly consisting of 6–12 cells in series. Generally, about 10–20% of the Ag was converted to AgCl, assuming 100% current efficiency.

Two solutions were used for chloridizing, 0.05 *N* KCl and 1*N* HCl, both electrolytes being readily obtained in a high degree of purity. The freshly prepared electrodes varied in color from almost white to dark brown.

*Aging and bias potential tests.*—The cell use for intra-comparison consisted of a 1-l flask modified to take the set of electrodes in a circle of short necks concentric to the neck of the flask. A slow stream of oxygen-free $N_2$ was introduced through the latter to agitate the bias solution. After chloridizing, the electrodes were removed from the U-tube cells, rinsed in de-ionized water, and transferred to the bias cell. All tests were carried out under a $N_2$ atmosphere in oxygen-free solutions.

To observe the time required for the potential to attain its equilibrium value, i.e., aging of the set of electrodes, the procedure of Smith and Taylor (4) was adopted. The new electrodes were measured relative to a set of two or more electrodes that had been aged for at least one week before use. Selection of the electrodes for the aged reference standards was arbitrary, guided only by the constancy (±0.005 mv) of the bias potential which was taken as a criterion of the stability of the equilibrated state.

Experimental data on the aging tests are summarized in Table I and illustrated in Fig. 1 and 2. Data in each case represent average values of at least three electrodes. The mass of thermal Ag was weighed to estimate quantitatively the AgCl formed in the next step.

The effect of increasing amounts of AgCl on the aging and stability of the electrodes was investigated. Since a constant current was used, each electrode had to be chloridized for a different length of time. This was accomplished by placing all the electrodes as before in the U-cells, but leading the current initially only through the

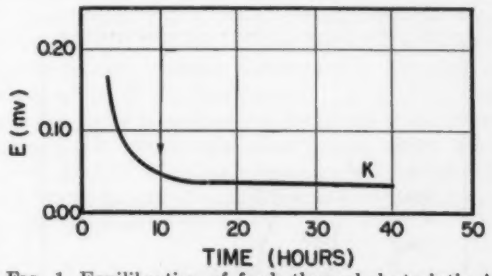


FIG. 1. Equilibration of fresh thermal-electrolytic Ag-AgCl electrodes (chloridized and aged in 0.05*N* KCl).

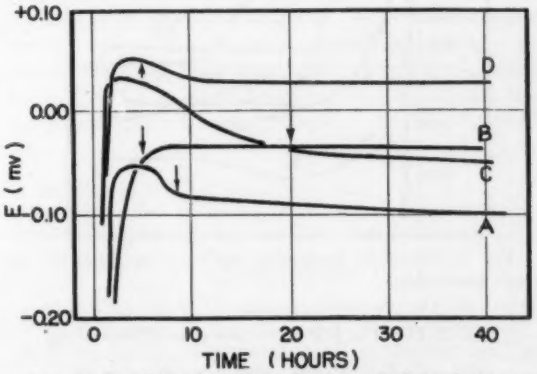


FIG. 2. Equilibration of fresh thermal-electrolytic Ag-AgCl electrodes (chloridized and aged in 1 and 0.1M HCl, respectively).

electrodes to be most highly chloridized. At proper time intervals, the current was lead through additional electrodes until the desired range of chloridizing had been achieved. In this manner, all the electrodes were in contact with the electrolyte for the same length of time and could be removed together so that the aging tests could be initiated on the set simultaneously. Results are summarized in Table II and illustrated in Fig. 3.

*Surface area measurements.*—Some measurements were undertaken to determine the porosity of the Ag in relation to its mass and the method of formation. As a first approximation, it was assumed that the surface area as determined by $N_2$ adsorption would be in direct proportion to the porosity of the surface. A B.E.T. adsorption apparatus of standard design (7) was used. Samples of thermal Ag were prepared on Pt spirals simultaneously with the electrodes selected for chloridizing by severing the beads from the glass electrode holder. Ag was deposited both in one and in two applications. The weight of Ag sphere for the single and double coats and the total weight of Ag

TABLE II. *Effect of increasing* AgCl *on equilibration of fresh electrodes*

| Electrodes | α | β | γ | δ | ε |
|---|---|---|---|---|---|
| | (Double Coats of Silver) | | | | |
| Wt of Ag (g) | 0.1214 | 0.3645 | 0.1810 | 0.1737 | 0.1165 |
| AgCl (%) | 16.2 | 20 | 30 | 50 | 90 |
| Equilibrium Time (hr) | 8 | 10 | 8 | 18 | 21 |

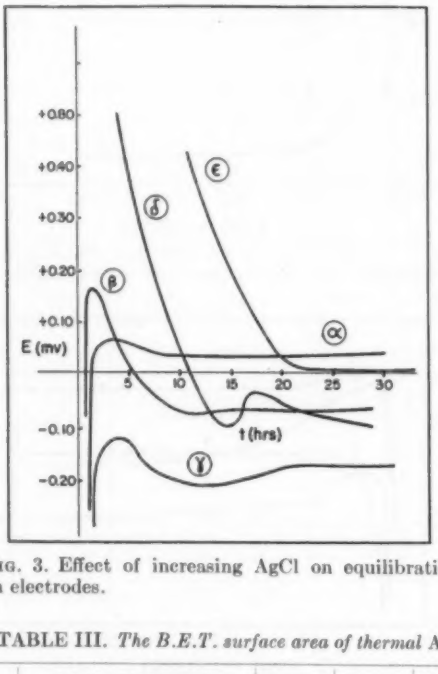


FIG. 3. Effect of increasing AgCl on equilibration of fresh electrodes.

TABLE III. *The B.E.T. surface area of thermal* Ag

| Sample | Wt (g) of Ag/electrode | | | Total wt (g) of sample | Surface area ($m^2/g$) | Equilibrium Time (hr) |
|---|---|---|---|---|---|---|
| | First coat (avg) | Second coat (avg) | Sum | | | |
| 1 | 0.0406 | None | 0.0406 | 0.4464 | 3.4 | 15 |
| 2 | 0.0321 | None | 0.0321 | 0.1925 | 39 | 150 |
| 3* | 0.1422 | None | 0.1422 | 1.1378 | 1.2 | 8 |
| 4 | 0.0441 | 0.0151 | 0.0592 | 2.7805 | 0.3 | 6 |

* This sample was degassed at 400°C for 17 hr. All others were degassed at 120°–150°C for periods up to 18 hr.

taken for each experiment is summarized in Table III together with the results of the measurements. The equilibration times refer to aging periods for electrodes prepared from thermal Ag of the surface areas listed.

Degassing of samples prior to determination of the adsorption isotherm was carried out by heating for 90 min under a high vacuum when $4 \times 10^{-5}$ mm Hg was attained (that of the system alone). Because of the heating at 450°C. during preparation, this was sufficient. Owing to the relatively small surface areas, the initial dose of $N_2$ to the sys had to be restricted to 8–10 mm pressure for successful measurements.

## DISCUSSION

The recommendations of Smith and Taylor (4) and Bates (3) for preparation of the thermal-electrolytic Ag-AgCl electrode for precision use have been independently checked and confirmed. Electrodes are readily obtained equilibrating to constant values within a period of 10–24 hr and showing an agreement of ±0.02 mv within a set prepared at a given time.

The aging histories show that when the chloridizing and aging solutions were of the same strength (Fig. 1), freshly prepared electrodes were positive in potential to the aged reference standards as predicted by the theory of concentration-polarization (4). Data for the experiments in which the chloridizing was continued until approximately 90% of the Ag was AgCl are informative (Fig. 3, Table II). In this work, the chloridizing solution (1*N* HCl) was ten times more concentrated than the bias test solution. Freshly prepared electrodes with greater than 30% AgCl were positive to the reference standards, in accord with a depletion of the electrolyte concentration to a strength less than that of the bias solution. The electrodes with less than 30% AgCl were initially negative. It follows that with shorter periods of electrolysis, depletion of electrolyte within the porous Ag is not sufficient to attain a concentration less than that of the bias test solution.

Minima and maxima have been observed in the aging history during the initial approach to equilibrium. Since the adjustment of the electrolyte concentration within the pores is a rate process, some fluctuations about the equilibrium value are not unexpected.

Results of the investigation of the dependence of equilibration time on electrode porosity are summarized in Table III. Electrodes with relatively high surface area (39 $m^2/g$) aged in 120–160 hr in contrast to low surface area electrodes (0.3–3.4 $m^2/g$) for which the period was as short as 6 hr. Application of the Ag in two coats effected this decrease.

When the initial application yielded a relatively nonporous thermal Ag (e.g., 3.4 $m^2/g$), the aging period was quite short (8–20 hr). Application of a second coat of Ag to this surface to obtain a still less porous surface (0.29 $m^2/g$) decreased the aging period only by a slight amount.

Results of these measurements leave little doubt that the role of the second coat of thermal Ag, as recommended by Bates (3), is to yield a less porous surface for chloridizing, leading to electrodes that equilibrate rapidly.

Surface areas and aging periods for single coats decreased markedly as the mass of thermal Ag was increased above 30 mg. If significant, this suggests that rapidly equilibrating electrodes can be achieved in one application of $Ag_2O$ if the electrode is made sufficiently massive. Bates (5) suggests that about 150–200 mg Ag be used.

Aging tests with increasing AgCl content (Fig. 3) showed that the best Ag-AgCl electrodes were obtained when electrolysis was controlled to change about 10–20% of the Ag to AgCl (assuming a current efficiency of 100%). Electrodes having less AgCl (5%, Fig. 2), and somewhat more (30%, Fig. 3) were still quite satisfactory from the viewpoint of rapid equilibration and sensitivity. Increasing AgCl much above this limit of 20% (e.g., 50 and 90%) re-

sulted in a thick coat of AgCl which added little to stability and tended to make the electrode more sluggish. A current of 10 ma was recommended (3) for the electrolysis, but lower currents (1 ma) were just as effective if the total time of electrolysis was increased accordingly. Use of currents greater than 10 ma was not investigated in the present work.

It was observed that, with 1*N* HCl as the chloridizing electrolyte, the electrodes were occasionally brown or plum colored, although utmost care was given in each step of the procedure as described. Normally, the electrodes were dirty white to light brown. Bates reported (8) that with repeated use of this chloridizing solution, light gray and even white, rather than brown, electrodes were obtained and recommends that the initial chloridizing solution be used repeatedly until the conductance is too low for the operation. The highly colored electrodes, while showing good intra-agreement in a set, tended to equilibrate at somewhat larger values (0.1–0.3 mv) relative to the aged reference standards. It may well be that pre-electrolysis of the chloridizing solution was beneficial in achieving conditions for the best electrodes. Work described elsewhere (4) showed that the electrode potential was not affected by light. Dark electrodes were also obtained in recent studies when more than 20% of the Ag was chloridized. In this case, the color may indicate that the chloride layer is heavier than desirable for good performance. It is of interest to note that the color of the best electrodes of the totally electrolytic type is, by contrast, a rose or plum shade rather than light gray or white (1). Factors affecting color are least understood.

An observation of the present work is that the new electrodes equilibrated at potentials both positive and negative to the reference standard at values significantly different (−0.08–+0.05 mv). This difference was not due to changes in the reference standard itself since two or more of the latter were observed to maintain a constant potential (±0.005 mv) for periods of several months. The explanation for these differences in equilibrated potentials is not obvious, but may be attributed in part to states of strain in the thermal Ag. The choice of the reference standard is made less arbitrary if electrodes having the lowest potential after equilibration are selected, corresponding to the lowest thermodynamic energy state.

Thus, while equilibrated electrodes showing intra-agreement of ±0.02 mv in a set are readily gained, the limits of reproducibility in equilibrated potential appear to be greater. In many measurements of concentration cells, this effect may be partially compensated for by using opposing electrodes from the same set and by interchanging electrodes. However, it may be of considerable significance in measurements where the standard potential of Ag-AgCl is involved.

Constancy of the equilibrated bias potential enables a correction to be applied to refer all emf values to a common energy level. The experimental scatter observed in measurements with this electrode may thus be partially reduced.

It is significant that the careful determination of the standard potential of the Ag-AgCl electrode in aqueous solutions by Harned and Ehlers (9) and more recently by Bates and Bower (10) differs by a small, but finite, value, 0.18 mv, at 25°C. The same type of electrode—the thermal-electrolytic—and a similar technique were employed. Activities of the HCl in these solutions were in agreement with each other as well as with other independent determinations (10). In the light of the present results, the reported difference in values for the standard potential may be partially attributed to the thermal-electrolytic type of Ag-AgCl electrode.

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# Degree of Dissociation from the Onsager Equation

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ABSTRACT

A new, analytical method is presented for calculating the degree of dissociation of weak, uni-univalent electrolytes from the Onsager equation. Also, the error involved in this procedure is discussed.

Various procedures have been published for the determination of the dissociation of weak, uni-univalent electrolytes from conductance data (1–5). In this paper, a noniterative method using the Onsager equation is derived.

The Onsager equation for a uni-univalent electrolyte is written as

$$\Lambda = \alpha(\Lambda_0 - (A + B\Lambda_0)\sqrt{\alpha c}) \qquad \text{(I)}$$

where $\Lambda$ = equivalent conductance, $\Lambda_0$ = equivalent conductance at infinite dilution, $A$, $B$ = constants, $c$ = concentration, $\alpha$ = degree of dissociation.

After rearranging, eq. (I) becomes

$$f(\alpha) = \alpha^{\frac{1}{2}}c^{\frac{1}{2}}k - \alpha\Lambda_0 + \Lambda = 0 \qquad \text{(II)}$$

where $k = (A + B\Lambda_0)$. If $\alpha_1$ is the first approximation of $\alpha$, so that $\alpha = \alpha_1 + h$, where $h$ is a constant, then expanding $f(\alpha)$ in a Taylor's series about $\alpha_1$ yields

$$f(\alpha) = f(\alpha_1) + hf'(\alpha_1) + h^2f''(\alpha_1)/2+ \qquad \text{(III)}$$

Assuming that the third term is small and may be neglected,

$$h_1 = -f(\alpha_1)/f'(\alpha_1) \qquad \text{(IV)}$$

so that the second approximation of $\alpha$ becomes

$$\alpha_2 = \alpha_1 - f(\alpha_1)/f'(\alpha_1) \qquad \text{(V)}$$

Eq. (V) is the same expression as that used in the Newton-Ralphson method.

Eq. (II) is now substituted in equation (V) and the value of $\alpha_1$ is taken as the conductance ratio, $\Lambda/\Lambda_0$ to give

$$\alpha_2 = \frac{\Lambda}{\Lambda_0} - \frac{(\Lambda/\Lambda_0)^{\frac{1}{2}}\, c^{\frac{1}{2}}\, k}{\frac{3}{2}(\Lambda/\Lambda_0)^{\frac{1}{2}}\, c^{\frac{1}{2}}\, k - \Lambda_0} \qquad \text{(VI)}$$

Although several rearrangements of the above equation are possible, the above form is very convenient for computation purposes.

It now becomes of interest to determine the error, $E$, in $\alpha$. The neglected terms of equation (III) form an alternating, convergent series. Consider the third term only. Obviously,

$$E = h - h_1 < f''(\alpha_1)h^2/2f'(\alpha_1) \qquad \text{(VII)}$$

It can be shown (6) that to a good approximation $h$ can be replaced by $h_1$ on the right side of eq. (VII). This conclusion also follows from the fact that the neglected terms are small.

In order to evaluate a useful expression for $E$, values of the derivatives are now substituted in eq. (VII), and it is assumed that $f'(\alpha) = -\Lambda_0$. Hence,

$$E < \frac{3c^{\frac{1}{2}}k}{8(\Lambda/\Lambda_0)^{\frac{1}{2}}\Lambda_0} \cdot h_1^2 \qquad \text{(VIII)}$$

Considering experimental conditions, the coefficient of $h_1^2$ is not greater than 1. Consequently,

$$E < h_1^2 \qquad \text{(IX)}$$

Thus, the number of significant figures in $h_1$ may be taken as the number of zeros between the decimal point and the first significant figure in the value of $h_1$.

It is also of interest to determine the dependence on $c$ of the ratios of $h_1/\alpha_1$ and of $E/\alpha_2$, i.e., the relative correction and the relative error.

The approximation is now introduced that

$$\alpha_1^2 = K/c \qquad \text{(X)}$$

where $K$ = the dissociation constant of the electrolyte. By use of the value of $h_1$ in equation (VI), modified by the above simplification of $f'(\alpha_1)$ and with the aid of equation (X), it is found that

$$h_1/\alpha_1 \cong -(kK^{\frac{1}{2}}/\Lambda_0)c^{\frac{1}{2}} \qquad \text{(XI)}$$

The relative error, calculated by suitable combination of the value of $h_1$, eq. (VIII), (X), and (XI) is given by

$$E/\alpha_2 < \frac{3k^2K^{\frac{1}{2}}}{8\Lambda_0^2(1 + kK^{\frac{1}{2}}\, c^{\frac{1}{2}}\, \Lambda_0)} \cdot c^{\frac{1}{2}} \qquad \text{(XII)}$$

where the term in parentheses is the ratio $\alpha_2/\alpha_1$.

From eq. (XII), it follows that the relative error is negligibly small at all practical values of $c$.

As a typical example, the conductance data of MacInnes and Shedlovsky (3) at low, intermediate, and high concentrations of acetic acid in water at 25°C are used to demonstrate the adaptability of eq. (VI). Since $A = 60.20$, $B = 0.229$, and $\Lambda_0 = 390.59$, it follows that $k = 149.65$. The necessary data are listed in Table I. Considering the rule stated above for the magnitude of the error, it will be observed that the formula for $\alpha_2$ holds over all the concentra-

TABLE I. *Conductance data of aqueous acetic acid solution*

| $c$ | $\Lambda$ | $\alpha_1$ | $-h_1$ | $\alpha_2$ (eq. VI) | $\alpha_2$ (Ref. 3) |
|---|---|---|---|---|---|
| 0.000028014 | 210.32 | 0.53847 | 0.0008031 | 0.53927 | 0.53925 |
| 0.0010283 | 48.133 | 0.12323 | 0.0005348 | 0.12376 | 0.12375 |
| 0.100000 | 5.200 | 0.013313 | 0.0001901 | 0.01350 | 0.01350 |
| 0.230785 | 3.391 | 0.0086817 | 0.0001528 | 0.008834 | 0.008827 |

tion range. At high concentrations, the formula will not be expected to give results agreeing with published values, since the simple Onsager equation will not be valid due to dimerization of the acid (7, 8).

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# Current Distribution in Galvanic Cells Involving Natural Convection

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ABSTRACT

From equations for mass transfer due to natural convection in a laminar boundary layer, it is derived that, in electrolytic cells used for the refining of metals such as Cu, the current density is virtually constant, although concentration polarization at both the cathode and the anode varies from bottom to top.

When a metal is deposited at a cathode, the steady-state concentration of cations in the solution next to the cathode is lower than in the bulk solution. Conversely, the steady-state concentration of cations in the solution next to the anode is higher than in the bulk solution. The resulting density difference between boundary layer and bulk solution brings about an upward or downward flow of the solution next to the electrode, analogous to natural convection for heat transfer. The effective thickness of the boundary layer is zero at the leading edge of the electrode where the flow of the solution originates, and increases with increasing distance from the leading edge.

Solutions of the boundary layer equations are available for the following conditions.

1. If an appropriate potential is applied to a cell containing a $CuSO_4$ solution, all Cu ions arriving at the cathode are readily discharged, but no other electrode reaction, such as evolution of $H_2$, may take place. Under these conditions, cation concentration at the electrode is virtually equal to zero, and the current reaches a limiting value $I_{max}$. Approximate solutions of the differential equations for the concentration and the velocity distribution in the boundary layer have been obtained by using solutions for the analogous heat transfer problem (1–7). For a laminar boundary layer, the local limiting current density is proportional to the fourth root of the distance from the leading edge of the electrode in accord with experimental results (3, 5–7).

2. If the applied current is lower than the aforementioned limiting current, concentration of cations discharged at the electrode is finite. The following limiting cases may be considered.

(*A*) The single electrode potential of the cathode and the anode may be assumed to be constant. Thus, if only concentration polarization occurs, the cation concentration at each electrode is constant, and the solution worked out for case 1 may be used with a slight modification. Accordingly, the local current density would be inversely proportional to the fourth root of the distance from the leading edge of the electrode.

(*B*) The current density may be essentially constant. This implies that the local concentration gradient at the surface of the electrode is constant, whereas the cation concentration at the electrode varies with the distance from the leading edge. In this case, the concentration difference between the bulk solution and the surface of the electrode is proportional to the fifth root of the distance from the leading edge of the electrode as follows from the analogy between heat and mass transfer (8).

In cells involving Cu electrodes and a solution of $CuSO_4$ as electrolyte, Wagner (3) and Ibl, Ruegg, and Trümpler (6) found experimentally that current density is virtually constant if the applied current is less than $\frac{1}{3}$ the limiting current for exclusive cathodic deposition of Cu. In what follows it is shown theoretically that this is expected to be true under most conditions.

As a special case of practical importance, a galvanic cell used for the refining of Cu is considered. Electrodes of height $h$ at a distance $s$ from each other are supposed to fill the cross section of the trough completely so that no edge effects occur and the primary current density would be constant.

It is assumed tentatively that the current density is virtually uniform, and conditions under which this assump-

tion is valid are investigated below. For a uniform current density $J$, the conventional form of Ohm's law may be used. If the potential-current density curve for the cathode and the anode are approximately linear,

$$\Delta\phi = E - J\,|\,dE_c/dJ\,| - J\,|\,dE_a/dJ\,| = Js/\sigma \quad \text{(I)}$$

where $\Delta\phi$ is the potential difference within the solution between cathode and anode, $E$ is the voltage applied to the cell, i.e., the potential difference measured between metallic terminals connected with the electrodes, $\sigma$ is the electrical conductivity of the electrolyte, $s/\sigma$ is the resistance of the electrolyte for a cross section of 1 cm², and $|\,dE_c/dJ\,|$ and $|\,dE_a/dJ\,|$ are the absolute values of the slopes of the potential-current density curves for the cathode and the anode, respectively.

Solving Eq. (I) for $J$,

$$J = \frac{E}{s/\sigma + |\,dE_c/dJ\,| + |\,dE_a/dJ\,|} \quad \text{(II)}$$

From Eq. (II), it follows that the current density will be essentially constant if the variation of the sum of the two terms

$$|\,dE_c/dJ\,| + |\,dE_a/dJ\,|$$

with distance $x$ from the lower edge of the electrodes is small in comparison to the total value of the denominator in Eq. (II). In what follows it is shown that this is the case under conditions which are most likely to be encountered in industrial cells.

Considering only concentration polarization and disregarding the difference between activities and concentrations, the following is obtained from Nernst's formula

$$\left|\frac{dE_c}{dJ}\right| = \frac{RT}{2\mathbf{F}}\left|\frac{d\ln c}{dJ}\right| = \frac{RT}{2\mathbf{F}}\frac{1}{c_0}\left|\frac{d\Delta c}{dJ}\right| \text{ if } |\Delta c| \ll c_0 \quad \text{(III)}$$

where $c$ is the concentration of Cu ions at the cathode, $c_0$ is the bulk concentration, and $\Delta c$ is the concentration difference between the bulk solution and the surface of the electrode.

Using the analogy between heat and mass transfer problems, the value of $\Delta c$ may be calculated in the same way as the temperature difference between a wall and an ambient fluid for a uniform heat flow per unit area has been calculated (8). Hence the value of $\Delta c$ at distance $x$ from the leading edge of the electrode is found to be

$$|\Delta c| = 1.62\,\frac{jx}{D}\,\frac{0.8 + Sc}{Sc^2\,Gr_x^*} \quad \text{(IV)}$$

where $j$ denotes the rate of mass transfer of Cu ions in mole/unit area/unit time due to diffusion, which is related to the current density by

$$j = J(1 - t)/2\mathbf{F} \quad \text{(V)}$$

where $\mathbf{F}$ is the Faraday constant and $t$ is the transference number of Cu ions. Moreover, $D$ is the diffusion coefficient, and $Sc$ is the Schmidt number defined as the ratio of the kinematic viscosity $\nu$ to $D$. The modified Grashoff number $Gr_x^*$ is defined as

$$Gr_x^* = g\beta' j x^4/D\nu^2 \quad \text{(VI)}$$

TABLE I. *Numerical values in Eq. (II) and (VIII)*

| $\frac{x}{h}$ | $\left\|\frac{dE_c}{dJ}\right\| + \left\|\frac{dE_a}{dJ}\right\|$ (ohm cm²) | $\frac{s}{\sigma} + \left\|\frac{dE_c}{dJ}\right\| + \left\|\frac{dE_a}{dJ}\right\|$ (ohm cm²) |
|---|---|---|
| 0 or 1 | 0.24 | 67.74 |
| 0.01 or 0.99 | 0.34 | 67.84 |
| 0.05 or 0.95 | 0.37 | 67.87 |
| 0.1 or 0.9 | 0.39 | 67.89 |
| 0.2 or 0.8 | 0.40 | 67.90 |
| 0.5 | 0.42 | 67.92 |

where $g$ is gravitational acceleration and $\beta'$ is the rate of change in the natural logarithm of the density of the solution with the concentration of $CuSO_4$.

Since the Schmidt number $Sc = \nu/D$ in aqueous electrolytes is of the order of $10^3$, the approximation $0.8 + Sc \cong Sc = \nu/D$ may be used in Eq. (IV). On substituting Eq. (IV)–(VI) in Eq. (III), it follows that

$$\frac{dE_c}{dJ} = 1.62\,\frac{4}{5}\,\frac{RT}{2\mathbf{F}}\,\frac{(1-t)^{\frac{1}{3}}\,x^{\frac{1}{3}}}{2\mathbf{F}Dc_0}\left(\frac{2\mathbf{F}\nu D^2}{gJ\beta'}\right)^{\frac{1}{3}} \quad \text{(VII)}$$

An analogous equation with $x' = h - x$ as the distance from the upper end of the electrode holds for the anode. Hence,

$$\left|\frac{dE_c}{dJ}\right| + \left|\frac{dE_a}{dJ}\right| = 1.62\,\frac{4}{5}\,\frac{RT}{2\mathbf{F}}\,\frac{(1-t)^{\frac{1}{3}}\,h^{\frac{1}{3}}}{2\mathbf{F}Dc_0} \cdot \left(\frac{2\mathbf{F}\nu D^2}{gJ\beta'}\right)^{\frac{1}{3}}\left[\left(\frac{x}{h}\right)^{\frac{1}{3}} + \left(\frac{h-x}{h}\right)^{\frac{1}{3}}\right] \quad \text{(VIII)}$$

Table I lists the results of a numerical evaluation of Eq. (VIII) for selected values of $x$ and the following values corresponding to experimental conditions used in an experiment by Ibl, Ruegg, and Trümpler (6) with 1.0M $CuSO_4$ as electrolyte: $R = 8.31$ joule/mole/degree; $T = 298°K$; $\mathbf{F} = 96{,}500$ coulombs/equivalent; $\sigma = 0.04$ ohm$^{-1}$/cm; $s = 2.7$ cm; $t = 0.3$; $J = 0.003$ amp/cm²; $D = 5 \cdot 10^{-6}$ cm²/sec; $g = 981$ cm/sec²; $\beta' = 150$ (mole/cm³)$^{-1}$; $h = 20$ cm; $\nu = 10^{-2}$ cm²/sec; $c_0 = 10^{-3}$ mole/cm³.

Table I shows that values of the denominator in Eq. (II) vary only slightly with distance $x$ since the first term $s/\sigma = 67.5$ ohm cm² exceeds by far the following terms accounting for polarization. Thus, the current density is found to be virtually uniform in accord with experimental results reported by Ibl, Ruegg, and Trümpler (6).

This result deduced for special conditions may be generalized. The following deviations from the foregoing presuppositions are to be considered.

1. If a supporting electrolyte, e.g., $H_2SO_4$ in addition to $CuSO_4$ is present, the density of the boundary layer is also affected by changes in the supporting electrolyte (3, 5). Thus, modifications of the foregoing equations are required, but the value of the right-hand member of Eq. (VIII) is not changed significantly. In addition, presence of a supporting electrolyte yields a higher conductivity corresponding to a smaller value of $s/\sigma$. Even for a ten times greater conductivity, however, values of the denominator in Eq. (II) at different heights differ by not more than 2½%.

2. In Eq. (VIII), activation polarization is disregarded. If activation polarization is considered, constant terms

on the right side of Eq. (VIII) have to be added. Thus, variation of the current density would be even smaller than has been estimated above.

3. Since the height $h$ of the cell occurs in Eq. (VIII) only as the fifth root, values other than $h = 10$ cm give essentially the same result.

4. The current density $J$ also occurs in Eq. (VIII) as the fifth root; therefore, different values of $J$ give qualitatively the same results. The condition of a nearly linear potential-current density curve, however, requires that $|\Delta c| \ll c_0$ according to Eq. (III). For the foregoing qualitative considerations, $|\Delta c| = \frac{1}{2} c_0$ may be used as an upper limit. In view of Eq. (IV) for $x = h$, $Sc \gg 0.8$, and the auxiliary Eq. (V) and (VI) the condition

$$J \leqq 0.55 \frac{\mathbf{F} D c_0^{\frac{1}{3}}}{1 - t} \left( \frac{g\beta'}{2\nu D h} \right)^{\frac{1}{3}} \qquad \text{(IX)}$$

is obtained for the validity of the foregoing considerations. It is obvious that, on increasing the current in a $CuSO_4$ cell, the solution at the cathode eventually becomes exceedingly depleted with respect to $CuSO_4$, and the limiting value of the current $I_{max}$ for exclusive cathodic deposition of Cu is approached. Under these conditions, Eq. (VIII) is not valid. Instead, the current density at the cathode is proportional to the fourth root of the distance from the lower edge as mentioned above.

5. The local current density would vary to a somewhat greater extent in a cell with a smaller width $s$, but such conditions are far from normal experimental conditions.

6. A large variability of the current density is expected in solutions involving a much lower value of $c_0$ than 1 mole/liter if the solutions contain a high concentration of supporting electrolyte which provides the same order of magnitude of the electrical conductivity assumed above. These conditions may be realized in a laboratory experiment (9), but do not occur in cells used for industrial refining of metals.

Consequently, as far as cells for industrial refining of metals are concerned, the current density is expected to vary only slightly from bottom to top of a cell, regardless of changes in the aforementioned parameters, provided the applied current is only a fraction of the limiting current for exclusive cathodic deposition of metal, i.e., the current density is lower than the value calculated in Eq. (IX).

Manuscript received May 28, 1956.
Any discussion of this paper will appear in a Discussion Section to be published in the December 1957 JOURNAL.

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## MANUSCRIPTS AND ABSTRACTS FOR FALL MEETING

Papers are now being solicited for the Fall Meeting of the Society, to be held at the Statler Hotel in Buffalo, N. Y., October 6, 7, 8, 9, and 10, 1957. Technical Sessions will be scheduled on Batteries, Corrosion, Electrodeposition (symposium on "Metal Powders"), Electrodeposition—Corrosion (Joint Symposium on "Corrosion of Electrodeposited Metals"), Electro-Organics, and Electrothermics and Metallurgy.

To be considered for this meeting, triplicate copies of abstracts (*not to exceed 75 words in length*) must be received at Society Headquarters, 216 West 102nd St., New York 25, N. Y., *not later than June 1, 1957. Please indicate on abstract for which Division's symposium the paper is to be scheduled.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.

* * *

The Spring 1958 Meeting will be held in New York City, April 27, 28, 29, 30, and May 1, 1958, at the Statler Hotel. Sessions will be announced in a later issue.

# FUTURE MEETINGS OF

# The Electrochemical Society

## Washington, D. C., May 12, 13, 14, 15, and 16, 1957

**Headquarters at the Statler Hotel**

**Sessions will be scheduled on**
**Electric Insulation, Electronics (including Luminescence, Semiconductors, Thermionic Cathodes, Instrumentation, and Screen Application), Electrothermics and Metallurgy, Industrial Electrolytics, and Theoretical Electrochemistry (including a special symposium on electrolytes)**

* * *

## Buffalo, October 6, 7, 8, 9, and 10, 1957

**Headquarters at the Statler Hotel**

**Sessions will be scheduled on**
**Batteries, Corrosion, Electrodeposition (symposium on "Metal Powders"), Electrodeposition—Corrosion (Joint Symposium on "Corrosion of Electrodeposited Metals"), Electro-Organics, and Electrothermics and Metallurgy**

* * *

## New York, April 27, 28, 29, 30, and May 1, 1958

**Headquarters at the Statler Hotel**

* * *

## Ottawa, September 28, 29, 30, October 1, and 2, 1958

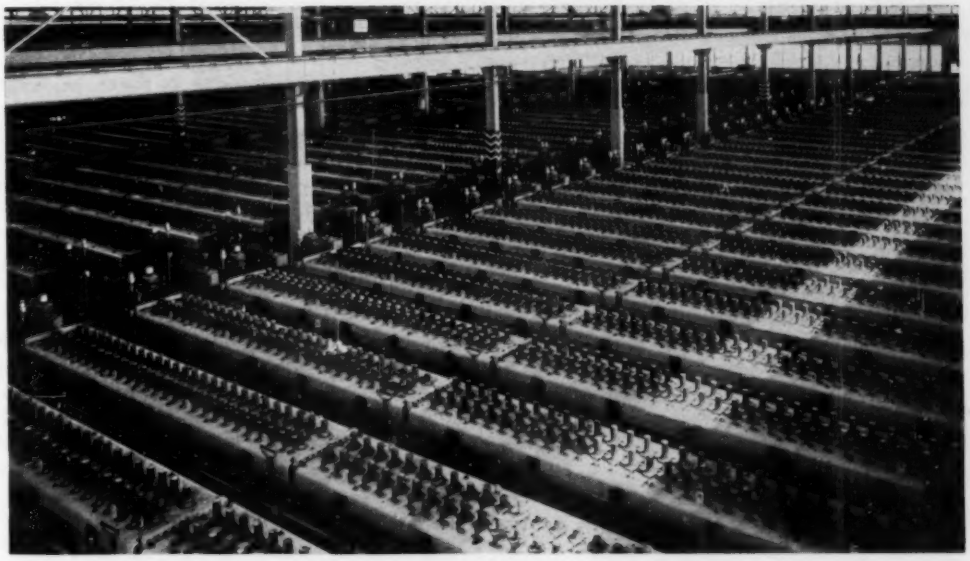
**Headquarters at the Chateau Laurier**

* * *

Papers are now being solicited for the meeting to be held in Buffalo, N. Y. Triplicate copies of each abstract (*not exceeding 75 words in length*) are due at the Secretary's Office, 216 West 102nd St., New York 25, N. Y., *not later than June 1, 1957* in order to be included in the program. *Please indicate on abstract for which Division's symposium the paper is to be scheduled.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.

# Current Affairs

## The Dow Chemical Co.—ECS Sustaining Member



View of chlorine cells at the Sarnia, Ont., Canada, plant of Dow Chemical of Canada, Ltd., a subsidiary of The Dow Chemical Co.

The ancestry of the long line of products manufactured today by The Dow Chemical Co., fourth largest in chemical production, extends well back into the earliest pages of its history.

Certainly no native of Midland, Mich., in 1890 would have dreamed that an old barn at the west end of Main Street housed the beginnings of a company that would some day turn out more than 600 chemical products.

A young chemist named Herbert H. Dow had journeyed that year to the small Michigan town on the banks of the Tittabawassee River. Dow, fresh from the Case School of Applied Science in Cleveland, felt sure that an underground salt sea in the area held rich potential for the future.

Dow was bent on testing, in particular, a method he had devised to extract bromine from underground brine, a process he felt to be considerably superior to others of the day. The bromine from Midland brines seemed to offer great promise, he had surmised, and it was there that he chose to work out his method.

Soon thereafter, through Dow's persistence and ingenuity as a chemist and engineer, bromine and later chlorine brought the establishment of a chemical company that was to grow into the large enterprise it is today.

The same Michigan brine also proved to be rich in sodium, calcium, and magnesium as well as bromine and chlorine. These five became the chemical "building blocks" that have led the company's parade of products, all of which stem from Herbert Dow's pioneering efforts.

Dow today is one of the pace-setters of a fast growing industry. The company has had a remarkable growth since its corporate birth May 18, 1897. Take the last 15 years, for example. Dow had experienced a thirteenfold growth in net property and a twelvefold increase in its sales since the beginning of World War II. Annual sales hit the $470 million mark in the fiscal year 1955.

Basic research, one of the fundamental factors that Herbert Dow instilled in his young company, has allowed Dow to expand continuously through the years. An average of more than 3% of the company's annual sales revenue is invested in its aggressive research activities.

From Dow's first humble setup in Midland, the organization has spread to locations throughout the country. At its Midland Division, the facilities are located in a 4000-acre area with 525 buildings atop rich brine deposits. Second largest of the installations is at Freeport, Texas, headquarters of the company's Texas Division. The company's third major production division, The Western Division, is located at Pittsburg, Calif., with facilities also at Seal Beach and Torrance, Calif.

Other plants are in Michigan, Connecticut, Massachusetts, Illinois, Colorado, Ohio, and Missouri. Subsidiary companies have home offices in Michigan, Oklahoma, Canada, The Netherlands, and Venezuela. Associated companies are in Michigan, Texas, and Maryland, with foreign associates in Japan, Wales, India, and Mexico. Moreover, Dow sales offices are located in 16 major cities of the country.

Today Dow and its subsidiaries employ approximately 25,000 people. In 1945 there were less than half this number of employees and in 1923 only about 1000.

Dow is one of the country's largest producers of bromine and chlorine. Surprisingly, however, little of either is sold commercially by the company, as the two are used as the basis of many of its chemical products. The company is a major supplier of caustic soda for many industrial uses; glycols for antifreeze and other products; industrial and drycleaning solvents; phenol for wood preservatives and for plastics; and many other industrial chemicals.

In addition to industrial, aromatic, and pharmaceutical chemicals, Dow is a prominent producer of agricultural chemicals, magnesium, and plastics.

Magnesium entered the Dow scene early in World War I. At that time its uses were largely wartime ones, and the recovery of the metal was accomplished from underground brines. Later, through development of alloys and methods for their fabrication, the company introduced magnesium to industry as a structural metal. It quickly became known as a great weight saver, the lightest of all structural metals.

In January 1941 Dow made significant strides in the scientific world with the pouring of the first ingot of magnesium extracted from sea water. The facilities at Freeport were set up to handle great volumes of ocean water, since the magnesium content in the sea is only 0.13%. Dow magnesium is now being entirely recovered from this vast source. Because of its abundance, lightness, strength, durability, and handling ease, the silvery white metal continues to find ever-increasing popularity in today's modern economy. Dow is the world's largest producer of the metal.

Today the opportunities for additions to Dow's line of products are greater than ever. Research continues to uncover new products as well as new uses for established ones.

Titanium is a good example. With Dow's prominence in the fields of magnesium and chlorine, it was only natural that the company should become interested in the growing uses for titanium. In the titanium process developed by William Kroll in 1937, magnesium is used as a reducing agent for titanium tetrachloride.

The current cost of obtaining the earth's ninth most abundant element from its ores has limited its usage, but development and progress to date have continued to raise its production. Dow has the capacity to turn out 1800 tons of titanium sponge annually, the terms of its present government contract, but the company's production has yet to reach this figure.

Only a few of the multitude of Dow products have been cited here. As time passes, the story continues to grow larger and larger. The continued emphasis on research and the valid philosophy that the spirit of a corporation is as animate as the spirit of its employees have been basic to the company since Herbert H. Dow founded it.

Maybe this is why The Dow Chemical Co. enjoys such an important place in industry today.

As a leader in the electrochemical field, The Dow Chemical Co. has taken an active part in the affairs of The Electrochemical Society, Inc., for many years, with members participating from the Midland, Texas, and Western Divisions and from the company's subsidiary, Dow Chemical of Canada, Ltd.

Dr. William R. Veazey, retired company director and formerly prominent in the company's research activities, served as Society President in 1946, and Dr. R. M. Hunter, staff coordinator of Dow Electrochemical activities, served in the same capacity in 1952. F. W. Koerker, technical expert with Electrochemical Planning at Midland, is serving on the Society's 1956 Board of Directors and as Chairman of the national Membership Committee. He is a former Chairman of the Council of Local Sections. Richard F. Bechtold of the Western Division at Pittsburg, Calif., was Chairman of the Society's national convention at San Francisco in the Spring of 1956.

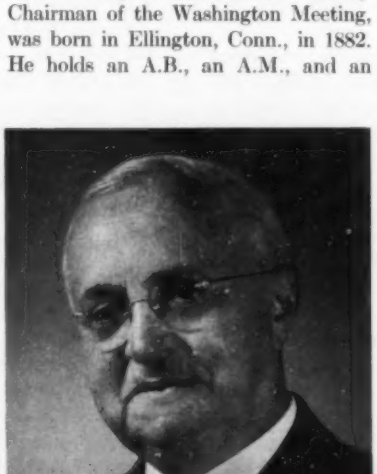
# Further Plans for Washington Meeting

The 111th Meeting of the Society will be held in Washington, D. C., May 12, 13, 14, 15, and 16, 1957. Convention Headquarters will be at the Hotel Statler, 16th St. at K & L Sts., N.W. The meeting will feature technical sessions sponsored by the Electric Insulation, Electronics (including Luminescence, Semiconductors, Thermionic Cathodes, Instrumentation, and Screen Applications), Electrothermics and Metallurgy, Industrial Electrolytic, and Theoretical Electrochemistry Divisions.

The complete program, including general information, technical sessions, and abstracts, will appear in the March JOURNAL.

Mr. Fielding Ogburn of the National Bureau of Standards is General Chairman of the meeting. Serving with him on the Steering Committee are J. Clark White, Vice-Chairman, Thomas D. Callinan, Walter J. Hamer, and Kenneth M. Huston. The committee chairmen appointed by Mr. Ogburn are: *Hotel*—Arthur G. Pierdon, *Finance*—John K. Taylor, *Registration*—Vernon A. Lamb, *Publicity*—Louis J. Frisco, *Laboratory Trips*—Ralph J. Brodd, *Entertainment*—Joseph F. Donahue, *Ladies' Program*—Mrs. Albert C. Simon.

Dr. George Wood Vinal, Honorary Chairman of the Washington Meeting, was born in Ellington, Conn., in 1882. He holds an A.B., an A.M., and an Honorary D.Sc. degree from Wesleyan University, Middletown, Conn.



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GEORGE W. VINAL

Dr. Vinal is known by all in the field of batteries for his many contributions which were made during his service with the Electrical Division of the National Bureau of Standards from 1908 until 1950, when he retired. His publications include some 25 technical papers and two text books on batteries.

Dr. Vinal's honors include, in addition to his Honorary Degree, membership in Phi Beta Kappa, the Gaston Planté Medaillé de la Société Française d'Electricité, a Certificate of the Office of Scientific Research and Development, Certificate of Commendation of the Navy Bureau of Ships, a Medal for Meritorious Service from the Department of Commerce, and The Acheson Medal.

Dr. Vinal is also a Fellow of the A.I.E.E. and the A.A.A.S., a member of the A.C.S., the Washington Academy of Sciences, the Philosophical Society of Washington, and the Cosmos Club.

Since his retirement from the Bureau of Standards, Dr. Vinal has served as a consultant to the Ray-O-Vac Co.,

The Electric Storage Battery Co., The Radio Corp. of America, and the E. J. Lavino Co.

Mrs. Vinal, Honorary Chairman of the Ladies' Committee, is a graduate of Eastern High School and Wilson Teachers' College in Washington, D. C. She taught in the elementary schools of Washington, D. C., for ten years prior to her marriage to Dr. Vinal in 1913.

Dr. and Mrs. Vinal are now living at Shelter Harbor, Westerly, R. I.

Washington Meeting Committee. *Left to right, standing*—Sidney M. Selis, Kenneth M. Huston, Louis J. Frisco, Walter J. Hamer, John K. Taylor, Ralph J. Brodd; *seated*—David Schlain, Gwendolyn B. Wood, Fielding Ogburn, D. T. Ferrell, Jr., Mrs. Albert C. Simon, Vernon A. Lamb.

### Laboratory Trips

Three laboratory trips have been arranged for this meeting. Participation in these trips must be arranged for, and transportation tickets purchased, at the time of registration.

*Monday, May 13, 1:15 P.M.*—Citizens of the United States attending the meeting will be conducted on a tour of the U. S. Naval Research Lab. in Washington. The radioactive cobalt facilities, the van de Graff installation, and the nuclear reaetor will comprise part of the tour. Also, the Electric Insulation Section, where work on the thermal evaluation of dielectrics is being carried on, will be shown. Finally, a visit to the Electrochemical Branch will be made to witness the work on batteries and gas detection. Transportation will be by chartered bus from the Sixteenth St. entrance of the Hotel Statler ($1.00). The estimated time of return to the Hotel is 4:30 P.M.

*Tuesday, May 14, 12:15 P.M.*—Citizens of the United States attending the meeting will be conducted on a tour of the U. S. Naval Ordnance Lab., White Oak in Silver Spring, Md. The guided tour will include visits to the Ordnance Environmental Lab., where experimental ordnance items are subjected to a variety of simulated conditions, such as shock, vibration, temperature and climate, and deep sea pressure; the Plastics and Battery Labs. and the Supersonic Wind Tunnels and Ballistic Ranges, where scale models are used in wide-range studies of the aerodynamic and physical problems encountered in extremely high speed flight. The visiting group will have lunch in the NOL cafeteria at the visitor's expense. Transportation will be by chartered bus from the Sixteenth St. entrance of the Hotel Statler ($1.00). The estimated time of return to the Hotel is 5:00 P.M.

*Wednesday, May 15, 1:30 P.M.*—There are no scheduled technical sessions for this afternoon. A tour of the National Bureau of Standards has been arranged (attendance will be limited to 200). The tour will begin with a short address by Dr. Wallace R. Brode, Associate Director of Chemistry. Immediately following the address the guests will visit various active research projects at the Bureau. Transportation will be by chartered bus from the Sixteenth St. entrance of the Hotel Statler ($1.00). The estimated time of return to the Hotel is 4:30 P.M.

### General Functions

Two evening social events are scheduled. On Monday, May 13, a get-acquainted Mixer will be held from 8:00 P.M. to 11:00 P.M. Beer, soft drinks, potato chips, and pretzels will be served. A bar will be available in the room for the purchase of mixed drinks. Those registered at the Meeting are invited to attend and renew old acquaintanceships, make new ones, and enjoy an evening of conversation.

The Society Luncheon and Annual Business Meeting will be held Tuesday, May 14, at 12:30 P.M.

A Reception for President and Mrs. Hans Thurnauer will be held on Tuesday May 14, at 6:30 P.M. Cocktails will be served from 6:30 P.M. to 7:30 P.M., followed by dinner at 7:30 P.M. President Thurnauer will then deliver the Presidential Address.

### Ladies' Program

A most interesting and entertaining program has been arranged for the ladies. The program, which was described in detail in the January JOURNAL, includes visits to Mount Vernon and the Custis-Lee Mansion in Alexandria, a tour of the Capitol, and a Fashion-Luncheon at the Mayflower Hotel.

Daily Coffee Hours will provide the opportunity to become acquainted and to arrange informal tours (both sightseeing and shopping), for which ample time has been alloted.

A Mixer on Monday evening and the President's Reception and Banquet on Tuesday evening are joint social functions which the ladies will not want to miss.

### General Information About Washington

Seven railroads offer direct service to Washington's Union Station, centrally located on the fringe of the downtown area. Just 15 minutes from the heart of the city, National Airport is serviced by ten airlines. Parkways, dual highways, and first-class through routes, many new and improved, converge on the Washington Metropolitan Area, making motoring to the city a pleasure.

Convention Headquarters will be located in the Hotel Statler, which is situated in the spacious downtown area. Arrangements have been made to provide accommodations in three additional hotels: the Ambassador, the Hamilton, and the Lee House, all within easy walking distance from the Statler.

Sight-seeing is Washington's leading attraction. The famous buildings and monuments, even within walking distance of hotel area, are too numerous to mention. The many museums, religious edifices, and gardens, rich in tradition, provide inspiration to hundreds of thousands of visitors each year. The opportunity to enjoy the best in cultural, historic, and artistic benefits, during a free hour, or a whole day, makes Washington, D. C., a favorite meeting place.

# A Behind-the-Scenes Look at the Cleveland Convention

*(With Ground Rules for Future Convention Committees)*

By edict, or the equivalent, there is held twice each year a National Convention of The Electrochemical Society. In 1956, what will be recognized as an unconventional convention conveniently convened in Cleveland, sponsored by the Cleveland Section, affectionately known in local circles as the National Carbon Division of the Society. The success of the convention was undeniably assured after all the available data were fed into R. W. ("Univac") Erwin, financial wizard of the local committee, who proceeded to grind out computations indicating our ability to meet expenses at any attendance level of registered members, nonmembers, guests, and outguesseds, and, further, he was able to show that if registration exceeded 289.6 (0.6 = 1 nonmember about to join) it would be feasible to consider having some technical sessions as well as the more enjoyable social privileges of mingling with the masses. Inasmuch as the attendance exceeded 950, there was thrown upon the section the added burden of providing facilities for would-be speakers who insisted on airing in public their favorite frustrations or meditations on problems obviously impossible to solve at this state of technical progress of the scientific intelligentsia, otherwise known as the cultured or mentally advanced. So, as you recall, technical sessions were included in the gross agenda—and, it might be added, some very provocative suggestions were brought to light. The slides shown were beyond question the most ingenious yet seen publicly and, in some cases, of most intricate design with delightfully straight lines and points of delicate and yet bold concept. It is regrettable, however, that the practically limitless medium of expression, i.e., color, was conspicuous by its absence. It should also be mentioned that certain most unusual effects were achieved by the more imaginative researchers by combining, indeed on a single chart, both curved and straight

TOP ROW—*left*, R. K. Shannon and H. B. Linford; *center*, Mrs. Veronica Acheson Mackey, H. A. Acheson, Mrs. Lyle Stuart, and Mrs. H. A. Acheson; *right*, R. M. Burns receiving Acheson Medal from President Hans Thurnauer. CENTER ROW—*left*, Mrs. Schafer, Shirley Ewing, and R. A. Schaefer; *center*, members of Cleveland Local Committee; *right*—Julian Glasser and Mrs. Lottie Fink, dancing. BOTTOM ROW—*left*, Mrs. Warner, J. C. Warner, H. R. Copson, and Frances Lang; *center*, C. E. Sample and Mr. and Mrs. U. B. Thomas; *right*, receiving line.

lines, though, unfortunately, the delineation of some of the most beautifully executed shaded spherical points was obscured by lines passing directly through them, suggesting a most careless attitude on the part of the scientist (if such a person can be called a scientist!).

Perhaps it does not fit best at this point, but it certainly should be mentioned that Cleveland must be considered a primitive city for there was more than casual evidence of the more popular brands of snake bite remedy; and there were known to be a number of rooms in the hotel (perhaps established for prompt handling of emergencies) where this remedy was being dispensed without charge by certain public-spirited industrial representatives to the more venturesome guests of the local section.

As you must know, if you have ever been involved in putting on a convention, such an affair practically runs itself. In spite of this, it is customary to organize a local committee with a chairman (purely an honorary post) and a number of subcommittees with imposing titles ostensibly related to the various categories of activity taking place. Such a committee, by time-honored and traditional precedent, must meet frequently, have reports, discussions, submit motions, vote, and occasionally turn down a suggestion so that it will not appear to be "railroading" (a detestable accusation). Actually, no suggestion need really be turned down, since it can be brought up again at the next meeting, when every one except the suggestee will have forgotten either the suggestion or the action taken (usually both), and favorable action assured (for it is well known that the actions of a committee are neither reproducible nor intelligible).

One subcommittee which always receives considerable attention is the Ladies' Committee which plans what to do with the ladies during the convention. This always surprises me—perhaps we have been too long with science.[1] But, well, let me ask just one question: If a convention is attended by 900 men and 50—yes, even 150—women, the women are going to constitute a problem? So much for the women's committee.

To make a long story short, rather than raise an unpopular question, Cleveland went along with the idea of a local committee, pretended to work hard (even accepted credit shamelessly and worse, publicly), honored the proper people, interfered with the hotel's work (only superficially), collected the money (all you do is sit at the table and people bring it to you), etc. All this in the name of the advance of science, beating back the frontiers of ignorance!

And now, are we content to let it drop? No, it must be reviewed again in the JOURNAL, and the many must read it and again do silent homage to the few who made this 110th convention possible—so that when it comes your turn to manage a convention, your praises may return, to be heaped upon your head with interest.

That the Convention in Cleveland was an outstanding success is shown by the following statistics:

Members, nonmembers, guests, total registration, ladies registered, students, maximum number of sessions going on simultaneously, average Cleveland temperature, anticipated profit, past presidents of Society attending, cost of tickets to Acheson Banquet, train fare to Ashtabula, number of 1-day registrants.

These numbers apply to above, but we have lost the order, so arrange to suit yourself:

16, 235, 460, 0.75, 200, 960, 11, 72°, 6.00, 4, 2004.00.

Certainly, some new records were set by this year's committee—records which we predict will stand unchallenged for some years.

CLEVELAND MEETING LOCAL COMMITTEE—*Anon.*

[1] A scientist (true scientist, that is) is defined as a man who believes he has found a subject more interesting than women.

Professor O. W. Brown, a Charter Member of the Society, deserves great credit for the interest Indiana University students have shown in electrochemistry. At the Cleveland Meeting, Professor F. C. Mathers listed 12 former students of theirs who were registered: L. I. Gilbertson, J. C. Warner, John Griess, Harry Gatos, C. V. King, H. Ricks, A. Fischbach, T. P. Dirkse, R. F. Koontz, G. R. Sherwood, J. A. Ricketts, and E. J. Ritchie.

# Highlights of the Meeting of the Board of Directors

*(Held September 30, 1956, Hotel Statler, Cleveland, Ohio)*

President Thurnauer presented the following list of Membership Committee representatives for Local Sections and Divisions: *Boston*—Richard Peak, *Chicago*—none, *Cleveland*—John Yeager, *Detroit*—Manuel Ben, *Midland*—R. S. Karpiuk, *New York Metropolitan*—Paul Howard, *Niagara Falls*—L. H. Juel, *Pacific Northwest*—M. J. Pryor, *Philadelphia*—F. X. McGarvey, *Pittsburgh*—E. A. Gulbransen, *San Francisco*—T. R. Beck, *Southern California-Nevada*—W. Hetherington, *Washington-Baltimore*—A. C. Simon, *Ontario-Quebec*—R. R. Rogers, *India*—M. S. Thacker; *Battery*—K. S. Willson, *Corrosion*—H. R. Copson, *Electric Insulation*—T. D. Callinan, *Electrodeposition*—R. A. Woofter, *Electronics*—F. J. Biondi and J. W. Faust, Jr., *Electro-Organic*—Hans Neumark, *Electrothermics and Metallurgy*—W. E. Kuhn, *Industrial Electrolytic*—W. J. Sakowski, *Theoretical Electrochemistry*—S. Schuldiner. These nominations were approved.

The appointment of the following representatives on other societies' committees also was approved: *ASA Committee C-18*—James M. Booe, *AIEE Committee C-40*—E. Willihnganz, *ASA Committee C-42*—W. C. Vosburgh, *ASA Committees Z-10 and Z-32*—W. J. Hamer.

Appointments to the Acheson Award Committee were approved: J. C. Warner, Chairman (term expires November 1957); addition of R. M. Hunter and E. M. Sherwood (terms to expire in November 1960).

*Report of the Treasurer.*—The report as given by L. I. Gilbertson was approved.

*Report of the Secretary.*—The Secretary turned the floor over to Dr. Ivor Campbell to describe a project that Dr. Campbell had undertaken on his own initiative—the preparation of an abstract of rules and regulations of The Electrochemical Society. Dr. Campbell and his colleagues have gone through the minutes of the meetings of the Board of Directors since about 1946 and have abstracted and codified the rules and regulations. Dr. Campbell

pointed out that this booklet will materially aid incoming Board members and he has presented copies, which are as yet tentative, awaiting corrections, additions, or deletions at the suggestion of the Board.

The Secretary announced that Mrs. Colin G. Fink had presented the Society with $1,074.40 in the form of stock in the Blue Ridge Mutual Co. The Board expressed its appreciation for this generous gift.

The Secretary was instructed to attend the forthcoming meeting of the Council of Engineering Society Secretaries in January 1957.

*Report of Ways and Means Committee.*—The Ways and Means Committee reported numerous changes in the Constitution and Bylaws. Some of the Bylaw actons are final, some are only the first rieading. It is the intent of the Society to publish in their entirety the revised Bylaws as completed at the January 1957 meeting of the Board. Also, the changes in the Constitution will be published prior to the Washington Meeting since a vote on these suggested changes will be taken at that time. Sections being revised concern: (*a*) adding Patrons to our classification of members, (*b*) the make-up of the Ways and Means Committee, making it a smaller committee, (*c*) deletion of the office of the Business Manager of the JOURNAL, giving these duties to the Secretary, (*d*) changing the fiscal year of the Society from January 1—December 31 to April 1—March 31, (*e*) creation of the office of Assistant Secretary, (*f*) clarification of representation of Sustaining and Patron Members, specifying that representatives otherwise eligible for Active Membership shall be considered Active Members.

*Report of Publication Committee.*—R. M. Burns, Chairman, commented on the growth of the JOURNAL from 1950 to 1956, and on the sale of the Society's monographs.

*Report of Finance Committee.*—The revised budget was approved (this is a 15-month budget covering the change in the fiscal year).

*Report of Membership Committee.*—F. W. Koerker, Chairman, gave an analysis of changes in membership from 1950 to 1956, commenting that as of September 1, 1956 there was an 8 to 10% increase thus far in the year depending on the number of in-process applications completed, and indications were that we would have well over 300 new members in the year.

*Report of Sustaining Membership Committee.*—The report of F. L. LaQue, Chairman of the Committee, was given. The Committee's activities have been successful; special emphasis has been placed on Patron Membership.

*Report of Council of Local Sections.*—The special report from the Council Subcommittee on Aiding Science in the High Schools was distributed to members of the Board for further study.

*New Business.*—H. H. Uhlig informed the Board of the progress he is making on arrangements for the International Symposium on Passivity. The Society agreed to an expenditure of up to $500 from Corrosion Division Monograph Funds for the publication of abstracts for this meeting.

HENRY B. LINFORD, *Secretary*

REVISED BUDGET 1/1/56-3/31/57

*Income*

| | Budget 15 mos. approved at San Francisco 4/29/56 | Revised Budget |
|---|---|---|
| All Membership Dues | $40,750 | $44,250 |
| Sustaining Memberships | 15,000 | 19,850 |
| Patron Memberships | | |
| Reprints | 5,000 | 5,000 |
| Nonmember Journal Subscriptions | 27,500 | 32,300 |
| Office Sale Journal & Publications | 1,250 | 1,250 |
| Advertising | 17,500 | 16,000 |
| Bound Volumes | 2,000 | 2,000 |
| Conventions | 5,000 | 3,500 |
| Membership Directory | 400 | 400 |
| Cathodic Protection Sales | | 250 |
| | $114,400 | $124,800 |
| Nonmember Journal Subscriptions | 5,440 | 5,440 |
| Nonmember Convention Registrations | 1,200 | 900 |
| Monograph Royalties | 1,560 | 5,500 |
| Income on Investments | | 500 |
| | $8,200 | $12,340 |
| Total | $122,600 | $137,140 |

*Expenses*

| | | |
|---|---|---|
| Printing & Mailing Journal | $44,750 | $44,750 |
| Reprints | 3,120 | 3,120 |
| Publication Committee | 440 | 440 |
| Advertising Commission | 6,500 | 6,500 |
| Salaries | 46,750 | 48,750 |
| Rent | 4,400 | 3,000 |
| Postage, Supplies, & Miscellaneous | 7,715 | 7,715 |
| Local Sections & Divisions | 1,250 | 1,250 |
| Young Author's Prize | 100 | 100 |
| Reserve New Office Equipment | 536 | 536 |
| Bound Volumes | 2,000 | 2,000 |
| Membership Directory | 750 | 750 |
| Convention: | | |
| Program Booklet | 1,380 | 1,580 |
| Travel of N. Y. Personnel | 1,500 | 1,700 |
| Materials & Supplies | 320 | 320 |
| Postage & Express | 490 | 490 |
| Total Estimated Expenses | $122,001 | $123,001 |
| Contingency 1% of Estimated Income | | 1,248 |
| Total | $122,001 | $124,249 |
| Excess Income Over Expenses General Fund | −7,601 | +551 |
| Income Credited to Society Reserve Fund | +8,200 | +12,340 |
| Net Excess Income Over Expenses | +599 | +12,891 |

## DIVISION NEWS

### Semiconductor Mailing List

The mailing list for the Semiconductor Symposia is being revised. Persons who are not already on the list but would like to be are requested to send their

names and addresses to Dr. J. W. Faust, Jr., Westinghouse Research Labs., Beulah Rd., Churchill Boro., Pittsburgh 35, Pa.

### Joint Symposium on Electroplated Coatings

Under the joint auspices of the Corrosion Division and the Electrodeposition Division, a symposium is being planned on the subject "The Corrosion Resistance of Electroplated Coatings" to be held in conjunction with the October 1957 Buffalo Meeting of the Society. Papers are being solicited for this symposium. They may be of three general types: (*a*) theoretical discussion of the mechanism of corrosion as it pertains specifically to electroplated coatings, (*b*) factual papers giving new or unpublished data on the performance of various electroplated coatings, (*c*) critical reviews of already published data. Papers on other subjects which are relevant to the topic of the symposium will also be welcomed.

In addition to submitting papers or abstracts through the usual channels to the Secretary of the Society, authors who wish to contribute to this symposium are asked to communicate with either Dr. H. Copson, International Nickel Co., P. O. Box U, Bergen Point Station, Bayonne, N. J., or Dr. F. A. Lowenheim, Research Lab., Metal & Thermit Corp., P. O. Box 471, Rahway, N. J.

## SECTION NEWS

### Chicago Section

The Chicago Section was privileged to have as its speaker on Capacitor Night, November 2, 1956, Mr. David B. Peck of the Research and Engineering Dept., Sprague Electric Co., speaking on "Electrochemical Aspects of Electrolytic Capacitors." The meeting was held at the Chicago Engineers Club.

Mr. Peck began his talk by tracing the development of the electrolytic capacitor from its beginnings in Germany over 50 years ago. He stated that the solid tantalum capacitor will replace the paper capacitor because it is smaller, has better high frequency characteristics, is less sensitive to temperature, and can be made for the same price. However, it must be operated in the low voltage range (20 v). An active discussion followed the presentation and Mr. Peck showed examples of some capacitors.

WILLIAM H. COLNER, *Secretary*

### Philadelphia Section

At the first regular meeting of the season on November 14, 1956, the Philadelphia Section was addressed by our national President, Dr. Hans Thurnauer, on the subject "Affairs of the National Society." He reported that the Society is in a good position financially, membership is increasing, and the quality of the Journal and meetings is improving.

The technical speaker of the evening was Dr. Armand Pansen of the Westinghouse Corp. who reported "The Temperature Dependence of Conductivity of Li and Li Salts in Anhydrous Methyl Amine."

HARRY C. MANDELL, JR.

### Pittsburgh Section

The second meeting of the year was held at the new research center of Jones & Laughlin Steel Corp. on October 12, 1956. After the local chairman Dr. A. Cornish opened the meeting, Dr. H. T. Clark, Research Director of Jones & Laughlin Steel Corp., described the company and the research laboratory. Then Dr. P. W. Blackburn of Westinghouse Research Labs. presented a paper on the crystallographic and the kinetic aspects of the oxidation of uranium dioxide. After an intermission, Dr. W. E. Wallace of the University of Pittsburgh presented a paper entitled "Studies of the Tantalum-Hydrogen System." Next, Dr. Marcel Bourgon of the University of Montreal presented a paper on "Electric Conductivity of Molten Cuprous Sulfide in Relation to Its Sulfur Activity." After lunch, Dr. R. Rice of Mellon Institute of Industrial Researches gave a talk on "Microstructures of Surfaces," followed by a paper by Mr. K. Andrew of Westinghouse Research Labs. on "Accelerated Oxidation of Metals and Alloys."

The meeting was ended with a tour of the laboratory arranged by Dr. R. Woofter.

LING YANG, *Secretary-Treasurer*

## NEW MEMBERS

In December 1956 the following were approved for membership in The Electrochemical Society by the Admissions Committee:

**Active Members Sponsored by a Patron or Sustaining Member**

ROBERT W. CAIRNS, Research Dept., Hercules Powder Co., Wilmington, Del. (Electro-Organic)

JOHN B. CAPUANO, Udylite Corp., 1651 E. Grand Blvd., Detroit 11, Mich. (Electrodeposition)

JOHN J. CARRONA, Tube Div., Radio Corp. of America, Harrison, N. J. (Electrodeposition, Electronics, Electrothermics & Metallurgy, Theoretical Electrochemistry)

DONALD E. COOPER, Titanium Metals Corp. of America, P. O. Box 2128, Henderson, Nev. (Electrothermics & Metallurgy)

RICHARD A. FELLOWS, Udylite Research Corp., 21441 Hoover, Van Dyke, Mich. (Electrodeposition)

FRANCIS E. MCKENNA, Air Reduction Co., Inc., Murray Hill, N. J. (Electrothermics & Metallurgy)

CHARLES B. MUNTON, National Cash

## JUNE 1957 DISCUSSION SECTION

A Discussion Section, covering papers published in the July–December 1956 JOURNALS, is scheduled for publication in the June 1957 issue. Any discussion which did not reach the Editor in time for inclusion in the December 1956 Discussion Section will be included in the June 1957 issue. Those who plan to contribute remarks for this Discussion Section should submit their comments or questions in triplicate to the Managing Editor of the JOURNAL, 216 W. 102nd St., New York 25, N. Y., *not later than March 1, 1957*. All discussions will be forwarded to the author, or authors, for reply before being printed in the JOURNAL.

## ECS Membership Statistics

The following two tables give breakdown of membership as of January 1, 1957. The Secretary's Office feels that a regular accounting of membership will be very stimulating to membership committee activities. In Table I it should be noted that the totals appearing in the right-hand column are not the sums of the figures in that line since members belong to more than one Division and, also, because Sustaining Members are not assigned to Divisions. But the totals listed are the total membership in each Section. In Table I, Sustaining Members have been credited to the various Sections.

TABLE I. *ECS Membership by Sections and Divisions*

| Section | Division | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Battery | Corrosion | Electric Insulation | Electro-deposition | Electronics | Electro-Organic | Electrothermics & Met. | Industrial Electrolytic | Theoretical Electrochem. | No Division | Total as of 1/1/57 | Total as of 1/1/56 | Net change |
| Chicago | 10 | 37 | 2 | 44 | 19 | 7 | 11 | 13 | 22 | 13 | 114 | 105 | +9 |
| Cleveland | 52 | 35 | 3 | 45 | 37 | 12 | 21 | 28 | 40 | 14 | 190 | 171 | +19 |
| Detroit | 7 | 19 | 5 | 38 | 5 | 8 | 3 | 4 | 21 | 21 | 85 | 73 | +12 |
| India | 6 | 3 | 1 | 13 | 3 | 5 | 3 | 11 | 6 | 3 | 27 | 23 | +4 |
| Midland | 5 | 15 | – | 4 | 2 | 2 | 6 | 16 | 8 | 3 | 41 | 38 | +3 |
| New York | 72 | 101 | 21 | 132 | 87 | 32 | 56 | 59 | 88 | 45 | 460 | 427 | +33 |
| Niagara Falls | 10 | 20 | 1 | 19 | 4 | 5 | 63 | 51 | 21 | 22 | 157 | 141 | +16 |
| Pacific Northwest | 5 | 16 | – | 11 | 1 | 1 | 6 | 11 | 7 | 8 | 51 | 40 | +11 |
| Philadelphia | 22 | 29 | 3 | 35 | 45 | 14 | 18 | 15 | 44 | 27 | 156 | 160 | −4 |
| Pittsburgh | 3 | 37 | 3 | 23 | 17 | 5 | 28 | 14 | 27 | 10 | 108 | 85 | +23 |
| San Francisco | 4 | 12 | 2 | 16 | 12 | 3 | 11 | 19 | 16 | 5 | 55 | 43 | +12 |
| Washington-Baltimore | 33 | 41 | 7 | 37 | 19 | 3 | 10 | 10 | 25 | 7 | 115 | 108 | +7 |
| Ontario-Quebec | 8 | 22 | – | 15 | 1 | 3 | 24 | 19 | 7 | 18 | 71 | 59 | +12 |
| U. S. Non-Section | 61 | 118 | 27 | 116 | 73 | 45 | 76 | 80 | 125 | 53 | 518 | 622 | −104 |
| Boston | 11 | 29 | 5 | 30 | 34 | 8 | 15 | 10 | 23 | 8 | 119 | 0 | +119 |
| Southern Calif.-Nevada | 13 | 16 | – | 18 | 13 | 3 | 8 | 12 | 12 | 9 | 63 | 0 | +63 |
| Foreign Non-Section | 40 | 50 | 7 | 57 | 23 | 26 | 33 | 57 | 61 | 56 | 204 | 175 | +29 |
| Total as of Jan. 1, 1957 | 362 | 600 | 87 | 653 | 395 | 182 | 392 | 425 | 553 | 322 | 2534 | | |
| Total as of Jan. 1, 1956 | 309 | 518 | 88 | 609 | 312 | 172 | 341 | 401 | 476 | 377 | | 2270 | |
| Net Change | +53 | +82 | −1 | +44 | +83 | +10 | +51 | +24 | +77 | −55 | | | |

TABLE II. *ECS Membership by Grade*

| | Total as of 1/1/57 | Total as of 1/1/56 | Net Change |
|---|---|---|---|
| Active | 2240 | 2013 | + 227 |
| Life | 15 | 14 | + 1 |
| Emeritus | 41 | 34 | + 7 |
| Associate | 38 | 49 | − 11 |
| Student | 61 | 53 | + 8 |
| Honorary | 5 | 5 | 0 |
| Sustaining | 134 | 102 | + 32 |
| Total | 2534 | 2270 | + 264 |

By action of the Board of Directors of the Society commencing January 1, 1956, all prospective members must include first year's dues with their applications for membership.

Also, please note that, if sponsors sign the application form itself processing can be expedited considerably.

Register Co., Main and K St., Dayton 9, Ohio (Electrodeposition)

WILLIAM M. STEINECKE, Research Dept., Bethlehem Steel Co., Bethlehem, Pa. (Electrothermics & Metallurgy)

JOHN J. TIERNEY, Brown, Lipe, Chapin Div. of General Motors Corp.; Mail add: R. D. #1, Grafton, Ohio (Electrodeposition)

ALEXANDER D. TURNBULL, Consolidated Mining & Smelting Co. of Canada Ltd.; Mail add: 300 Kootenay Ave., Trail, B. C., Canada

### Active Members

JAMES T. N. ATKINSON, Naval Research Establishment, c/o Fleet Mail Office, Halifax, N. S., Canada (Corrosion, Electrodeposition)

MYRON O. DAVIES, Western Reserve University; Mail add: 13436 Harlan Ave., Lakewood 7, Ohio (Battery, Theoretical Electrochemistry)

DON E. HARRISON, General Electric Co.; Mail add: 15998 Nelacrest Rd., Cleveland 12, Ohio (Electronics)

JAROSLAV HEYROVSKY, Polarographic Institute; Mail add: Vlasska 9, Mala Strana, Prahal, Czechoslovakia (Electrodeposition, Electro-Organic, Theoretical Electrochemistry)

ROBERT G. HUDSON, Carnegie Institute of Technology; Mail add: 316 E. End Ave., Pittsburgh 21, Pa. (Theoretical Electrochemistry)

HELEN M. JOSEPH, National Carbon Research Labs.; Mail add: 6415 Sunderland Dr., Parma 29, Ohio (Corrosion)

CLARENCE KARAN, International Business Machines Corp.; Mail add: 51 Kinry Rd., Poughkeepsie, N. Y. (Electronics)

ERICH KRAUTZ, Osram Co.; Mail add: Obere Lechdammstrasse 65, Augsburg, Germany (Electronics, Electrothermics & Metallurgy)

HENRY LEIDHEISER, JR., Virginia Institute for Scientific Research, 326 North Blvd., Richmond 20, Va. (Corrosion, Electrodeposition)

JOSEPH T. LIMERI, Electro Refractories & Abrasive Corp.; Mail add: 20 Fairchild Dr., Eggertsville 21, N. Y. (Electrothermics & Metallurgy)

WILFRIED MEYER, Osram Co.; Mail add: Bayernallee 21, Berlin-Charlottenburg 9, Germany (Electronics, Electrothermics & Metallurgy)

WILLIAM A. ROBERTSON, General Dry Batteries Co., Div. of P. R. Mallory & Co.; Mail add: 22420 Morton Ave., Cleveland 26, Ohio

ROBERT C. TAYLOR, Merck & Co., Inc.; Mail add: 189-02 64th Ave., Fresh Meadows, N. Y. (Electronics)

GORDON A. THOMAS, General Dry Battery Co.; Mail add: 16102 Edgecliff Ave., Cleveland 11, Ohio (Battery)

### Associate Member

ANTHONY J. SOLDANO, Sylvania Electric Products Inc.; Mail add: 78-25 19th Drive, Jackson Heights, N. Y. (Electronics)

### Reinstatements to Active Membership

FRANK P. GILLIGAN, Henry Souther Engineering Co.; Mail add: 11 Laurel St., Hartford 6, Conn. (Corrosion, Electrodeposition, Electrothermics & Metallurgy)

KARL G. SODERBERG, Chalmers Institute of Technology; Mail add: Kullagardsvaegen 6, Saevedalen, Sweden

**Transfer from Student Associate to Active Membership**

DONALD W. ERNST, National Bureau of Standards, Washington 25, D. C. (Electrodeposition)

**Transfers from Associate to Active Membership**

ROGER J. LABRIE, National Bureau of Standards; Mail add: 1308 New Hampshire Ave., Washington 6, D. C. (Electrodeposition)

JACOB M. MILLER, Armour Research Foundation, Technology Center, Chicago 16, Ill. (Corrosion)

ROBERT A. OSTERYOUNG, Dept. of Chemistry, Rensselaer Polytechnical Institute, Troy, N. Y. (Electrodeposition, Theoretical Electrochemistry)

ROMEO R. WITHERSPOON, National Carbon Research Lab.; Mail add: 1335 Mathews, Apt. 3, Lakewood 7, Ohio (Battery)

**Deceased Reported during November 1956**

FRANCOIS GALL, Le Chesney, Seine and Oise, France

WILLIAM W. HANSCOM, San Francisco, Calif.

HENRY G. ORLIK, Oaklyn, N. J.

HARVEY F. MACK, Easton, Pa.

## PERSONALS

STANISLAUS SKOWRONSKI has been placed on the Emeritus rolls after 50 years of membership in the Society. Prior to his retirement on July 1, 1956, he was with the Raritan Copper Works of the International Smelting and Refining Co. in Perth Amboy, N. J. He resides in Metuchen, N. J.

DONALD W. ERNST, a recent graduate of the University of Wisconsin, has joined the National Bureau of Standards, Washington, D. C., as an American Electroplater's Society Research Associate. He was a student member of the Chicago Branch.

DAVID STERN has been named Assistant Manager of the Whittier (Calif.) Research Lab. of the American Potash & Chemical Corp. Dr. Stern previously had been head of the research laboratory's electrochemicals section.

PHILIP J. CLOUGH has been appointed Director of the Metallurgical Research Dept. of the National Research Corp., Cambridge, Mass. He has been active in the company's extractive and process metallurgy program and in the development of metallic coating techniques. He holds numerous patents in these fields.

H. C. RIGGS has been named coordinator of missile applications engineering by the Exide Industrial Div. of The Electric Storage Battery Co., Philadelphia. Previously manager of Exide's engineering development division, Mr. Riggs now spearheads the company's expanded developmental program for the production of missile battery power units.

## NEWS ITEMS

### ECS Symposium on Electrolytes

The program for the Washington Meeting of the Society, May 12 to 16, 1957, will appear in the March issue of the JOURNAL. It will be noticed that the symposium on the Structure of Electrolytic Solutions (Electrolytes) scheduled for May 13, 14, and 15 was made possible by the joint sponsorship and generous financial support of the National Science Foundation, Washington, D. C., enabling the attendance at this meeting of leading authorities in various countries throughout the world.

### 8th Annual Dinner of Chemical Profession of Cleveland

Five Greater Cleveland chemists and engineers were honored by their fellows for their contributions to the chemical profession and the growth of their individual societies. The occasion was the Eighth Annual Dinner of the Chemical Profession in Cleveland, attended by some 300 chemists and chemical engineers, in the Manger Hotel.

Dr. John C. Warner, President of Carnegie Institute of Technology, President of the American Chemical Society, and Past President of The Electrochemical Society, addressed the gathering on, "Our Country's Most Paying Investment."

The Fourth Annual Award certificates were presented to: *Dr. K. S. Willson*, Manager of Research and Development, General Dry Batteries Co., nominated by the American Institute of Chemists; *Dr. E. C. Hughes*, Research Manager, Standard Oil Co. of Ohio, nominated by the American Chemical Society; *Dr. Paul S. Brooks*, Group Leader at National Carbon Co., nominated by Alpha Chi Sigma; *Dr. Thomas J. Walsh*, Professor of Chemical Engineering, Case Institute of Technology, nominated by the American Institute of Chemical Engineers; *Mr. Nelson C. Cahoon*, Group Leader at National Carbon Co., nominated by The Electrochemical Society.

The dinner was sponsored by the Cleveland Sections of the American Chemical Society, The Electrochemical Society, American Institute of Chemists, American Institute of Chemical Engineers, and Alpha Chi Sigma, the national professional chemists' fraternity.

### Winners of Warner Prize in Chemistry

The winners of the 1956–57 Warner Prize in Chemistry have been announced by Dr. Frederick D. Rossini, Head of the Dept. of Chemistry at Carnegie Institute of Technology.

The Warner Sophomore Prize went to John A. Olmsted, III, of Petaluma, Calif., and the Warner Senior Prize to Terry E. Sharp of LaCrosse, Wis.

The prizes were established by Dr. J. C. Warner, President of Carnegie Tech and former Head of the Dept. of Chemistry. The prize for sophomores consists of a three-year membership in the Student Affiliate Chapter of the A. C. S. and is awarded on the basis of scholastic record. The prize for seniors is a three-year membership to the A. C. S. and is given for both scholastic achievement and professional promise.

### Engineering Education Awards Offered

Seven national awards in engineering education will be given by the American Society for Engineering Education at its 1957 Annual Meeting at Cornell University, June 17–21. Competitions for all the awards are now open, and nomination blanks are ready.

The seven awards are:

1. The Lamme Award, given annually to an engineering educator for distinguished achievements contributing to the advancement of the profession.

2. The George Westinghouse Award, an annual $1000 prize for distinguished contributions to teaching engineering students.

3. The Vincent Bendix Award, a gold medal given annually for achievement in engineering research in colleges and universities.

4. The Curtis W. McGraw Research Award, a $1000 prize to be given for the first time, to honor young staff members

for contributions through engineering college research.

5. The James H. McGraw Award In Technical Institute Education, an annual prize of $500 presented for established achievement in technical institute education.

6. The President's Awards to Young Engineering Teachers, given annually for papers written by young engineering teachers, 36 years or younger, on a phase of engineering education. Prizes of $200 and $100 are given for the two top-ranking papers.

7. The Engineering Drawing Award of a certificate for distinguished service by a member of the Society's Engineering Drawing Division.

The Society's awards are given to winners selected, in each case, by special committees assigned to study the records of each nominee.

Further information and blanks for nominations are available from Professor W. Leighton Collins, Secretary of the Society, at the University of Illinois, Urbana, Ill.

## N.S.F. Science Grants

Grants totaling $4,065,000 have been awarded by the National Science Foundation to 16 colleges and universities in the United States to support academic-year institutes designed to help high school science teachers improve their knowledge of science subject matter.

In announcing the awards, Alan T. Waterman, Director of the Foundation, said that an estimated 750 high school science and mathematics teachers would be enrolled in the institutes which begin in September 1957. Each teacher will pursue a program of study in the sciences and mathematics planned especially for him and conducted by leaders noted not only for competence in their fields but for skill in presentation. The grants will provide stipends of $3000 each to approximately 50 teachers in each institute. Additional allowances for dependents and travel will also be provided.

"Our high school population is the heaviest it has ever been, and it is growing steadily," said Dr. Waterman. "The present supply of highly capable high school science and mathematics teachers, as well as the certain need for more of them in the near future, constitute the most critical and difficult problem in the effort to maintain an adequate supply of top quality scientists and engineers. This places a tremendous responsibility on today's high school science teachers. In order to help them, the Foundation is attempting to provide an opportunity for intensive training in the scientific subjects taught in high school through an enlarged program of academic-year institutes, established in colleges and universities widely scattered across the Nation."

Dr. Waterman pointed out that the teaching of science, mathematics, and engineering not only calls for specialized training but that advances in these fields are now so rapid that continuing effort must be made to keep teachers abreast of new developments.

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The National Science Foundation has announced 326 grants totaling $5,963,-724 awarded during the quarter ending September 30, 1956, for the support of basic research in the sciences, for conferences in support of science, for exchange of scientific information, for training of science teachers, and for the support for attendance of scientists at scientific meetings abroad. This is the first group of awards to be made during the fiscal year 1957.

The grants were made to institutions and scientists in 35 of the States, Canada, Hawaii, Israel, and Japan. The research fields included are anthropology, astronomy, chemistry, biological sciences, physics, earth sciences, engineering sciences, mathematical sciences, medical sciences, and socio-physical sciences.

## Symposium on Vacuum Technology

The Third National Symposium on Vacuum Technology was held in Chicago on October 10, 11, and 12, 1956. Sponsored by the Committee on Vacuum Techniques, the meeting attracted more than 500 representatives from industry, government, and university organizations which employ high vacuum processes.

Forty-two technical papers were presented covering Fundamental Developments in Vacuum Technology, Methods and Techniques for Obtaining High Vacuum, Instrumentation and Control of High Vacuum Equipment, Vacuum Distillation and Evaporation, Metallurgical and Chemical Applications, Vacuum Technology as Related to Atomic Energy, and Extraterrestrial Problems.

The technical papers will be published in a single volume as they have been for past meetings. The publications represent the latest, most concentrated assemblies of information in the high vacuum field.

The Committee on Vacuum Techniques, Boston, Mass., is a nonprofit organization supported by industries employing high vacuum processes, laboratories utilizing vacuum techniques in research, and manufacturers of high vacuum equipment.

## International Conference on Scientific Information

The National Science Foundation, the National Academy of Sciences—National Research Council, and the American Documentation Institute have announced joint sponsorship of an International Conference on Scientific Information to provide for a thorough discussion of present developments and research pertaining to the organization and dissemination of scientific information, with special emphasis on storage and retrospective search. The conference will be held in Washington, D. C., early in November 1958.

The conference objective is to attempt to overcome mounting difficulties in scientific communication resulting from the increasing tempo of research activity and the ensuing flood of scientific publications.

The subject matter to be covered will be grouped in the following general areas:

1. Requirements of scientists for scientific literature and reference services.

2. Function and effectiveness of abstracting and indexing services for storage and retrieval of scientific information and possible development of such services.

3. Effectiveness of scientific monographs, compendia, and specialized information centers for storage and retrieval of scientific information: survey of present practices, trends, and new and proposed techniques and types of services.

4. Organization of information for storage and retrospective search: comparative characteristics of existing systems.

5. Organization of knowledge for storage and retrospective search: conceptual and mechanical problems in the design of new systems.

6. Organization of information for storage and retrospective search: possible development of a general theory of storage and search.

7. Responsibilities of governmental bodies, professional societies, universities, and research and industrial organizations for research and training in scientific documentation and for operation of scientific information services.

The papers and an edited account of the discussions at the conference will be published in book form as the Proceedings of the Conference on Scientific Information.

Executive Secretary is Dr. Alberto F. Thompson, International Conference on Scientific Information, National Academy of Sciences—National Research Council, 2101 Constitution Ave., Washington 25, D. C.

## A.I.M.E. Names 1958 President

Following a meeting of the Board of Directors in New York, the American Institute of Mining, Metallurgical, and Petroleum Engineers has announced the election of Dr. Augustus B. Kinzel, of New York, as President for one year, beginning February 1958. Dr. Kinzel is Vice-President of Research for Union Carbide and Carbon Corp. where he has been actively engaged in research work for the past 30 years. His contributions have covered a wide range of activities in the fields of metallurgy, industrial gases, and atomic energy.

Grover J. Holt, of Ishpeming, Mich., General Manager of the ore mining department of The Cleveland-Cliffs Iron Co., now President-Elect, will take office on February 26 at the annual meeting to be held in New Orleans.

## E. C. Britton Retires

Edgar C. Britton has retired as Director of The Dow Chemical Co.'s Edgar C. Britton Organic Research Lab. at Midland but will continue to serve as a research consultant on a company-wide basis. He has been succeeded as laboratory director by Ralph P. Perkins, formerly an assistant director.

Dr. Britton, who received the Perkin Medal, industrial chemistry's highest award, in September 1956, will continue as a member of the company's Agricultural Chemicals executive committee and as a board member and secretary of Dow Corning Corp., a Dow associated company. He will retain an office in the laboratory bearing his name. A research group has been assigned to work on problems of special interest to him.

Dr. Perkins, who joined Dow in 1929, has been engaged in organic research during his entire career.

## Protective Coatings for Titanium

The National Bureau of Standards, Washington, D. C., has successfully electrodeposited hard, adherent protective coatings on titanium. The procedure involves forming a titanium fluoride film on the metal surface, electroplating with chromium, and heat-treating the plated specimen at 800°C. Developed for the Springfield Armory by C. L. Stanley and Abner Brenner of the Bureau staff, the process is expected to extend considerably the utility of titanium metal, particularly for high-temperature applications.

## New Engineering Center

United Engineering Trustees, Inc., has signed a contract for preliminary architectural plans and studies for a new Engineering Center in mid-Manhattan, New York City. This is the first definite step toward construction of what is expected to make New York the "engineering capital of the world."

The architects named are Shreve, Lamb and Harmon Associates of 11 E. 44th St., New York, designers of the Empire State Building and more recently the new Brooklyn Supreme Court Building. No details have been given as to specific location, cost, or time of completion.

It is believed that preliminary plans will be completed early this year. The inclination toward a mid-Manhattan site is due to appreciation of the accessibility of railroad and airline terminals and convention hotels.

## American Lithium Institute

Establishment of the American Lithium Institute, Inc., for the purpose of conducting research on lithium and its compounds, has been announced by the American Potash and Chemical Corp., Foote Mineral Co., and Lithium Corp. of America.

The Institute, a non-profit organization, will maintain offices in Princeton, N. J., including a technical library and literature service.

Marshall Sittig, formerly of the Ethyl Corp., has been elected President and Managing Director of the Institute.

Projects will be assigned to appropriate colleges and research institutions, but will be guided by the Institute's Technical Policy Committee, composed of representatives from the three member companies.

## RMI—Olin Mathieson Field Liaison Offices

Reaction Motors, Inc., and Olin Mathieson Chemical Corp. have announced the establishment of joint field liaison offices for RMI and the Olin Mathieson Aviation Div. in Dayton, Ohio, and Los Angeles, Calif. Both offices previously represented Reaction Motors.

The Dayton Office, newly located at 349 W. First St., is under the direction of G. Richard Lott. The Los Angeles office, located at 1373 Westwood Blvd., is under the direction of John M. Rogers, West Coast Manager.

## Sylvania-Corning Nuclear Corp.

Sylvania Electric Products Inc. and Corning Glass Works have announced a proposal to form a jointly owned company for the purpose of expanded research, development, and production activities in the atomic energy field. The new organization, to be known as the "Sylvania-Corning Nuclear Corp.," will be incorporated in Delaware, and Sylvania and Corning will each own one-half of the company's stock.

Sylvania's entire atomic energy business will become a part of the new company, and Corning will similarly transfer its atomic energy activities. Administrative headquarters and laboratories of the Sylvania division are located at the company's Research Center in Bayside, L. I., with pilot production facilities at Hicksville, L. I. Corning's activities are located at Corning, N. Y.

## New G.E. Test Facility

Procedures and equipment for refueling large boiling water reactors will be developed and proved in a new facility at the General Electric Co.'s Atomic Power Equipment Department in San Jose, Calif.

The new test facility was designed specifically for developing refueling procedures for the 180,000-kw Commonwealth Edison Dresden nuclear power station which General Electric will construct near Chicago. It also will be suitable for use with other boiling water type reactors.

## Arthur D. Little, Inc. Expansion

Plans for expansion in Cambridge and Concord of Arthur D. Little, Inc. were recently announced. The purchase of 170 acres in Concord and immediate new construction at Acorn Park in Cambridge were included in these plans.

A new wing has been completed at Acorn Park, the Arthur D. Little, Inc. laboratories in West Cambridge. A general purpose building is expected to be ready for occupancy in the fall. A large

tract in the West Concord area has been purchased, initially for the housing of an affiliate that was scheduled for Acorn Park, where all available space is now required by the parent organization.

The new wing at Acorn Park will help to relieve the pressure of recent staff growth by adding 30,000 square feet to house the ADL Flavor Lab. and the Chemical and Metallurgical Engineering Div.

Company officials are planning a new building of 40,000 square feet at Acorn Park to contain other expanding activities including technical economics and operations research. This new construction will also permit growth in other parts of the company.

Nuclear Metals, Inc., an affiliate, will probably be the first group to move to the new site. Preliminary plans for a modern laboratory building of 70,000 square feet give some idea of the affiliated company's need for more expansion than its present quarters in downtown Cambridge can provide. The new construction will bring research-based industries to this area.

## Copper Sulfate Production Capacity Increased

Republic Chemical Corp.'s copper Sulfate plant at Curtis Bay, Baltimore, Md., recently completed installation of equipment for expanded capacity. The total cost of the plant installation is approximately one million dollars.

An electric furnace for copper purification and most modern stainless steel filters, crystallizers, driers, screening and bagging, etc., make this plant a most modern and economical producer of copper sulfate.

## Radiation Studies on Plastics and Insulation

The American Society for Testing Materials has announced the formation of a subcommittee to study the effects of nuclear and high energy radiation on the properties of plastics and electrical insulation. Chairman of the new subcommittee is D. S. Ballantine of Brookhaven National Lab. At the first meeting of the group, the chairman emphasized the great need for standardization in the field of radiation effects and the timeliness of ASTM's decision to form such a committee. The data already existing in the field of radiation effects on materials are in many cases confusing, and instances of outright contradictions are not uncommon.

It is the prime objective of this new subcommittee to establish, where possible, standard methods of irradiation and standard methods for determining the effects of radiation on the physical and chemical properties of plastics and electrical insulation. The subcommittee on radiation effects sponsored jointly by ASTM Committee D-20 on Plastics, F. W Reinhart, Chairman, and D-9 on Electrical Insulating Materials, H. K. Graves, Chairman, has established sections to work in the following areas: (*a*) nomenclature and definitions, (*b*) dosimetry, (*c*) correlation of various sources of radiation, (*d*) total dosage and dose-rate effects, and (*e*) post irradiation effects.

Anyone interested in assisting the work of this committee is invited to write to the chairman, D. S. Ballantine at Brookhaven National Lab., Upton, N. Y.

## Middle East Desalting Plant

The largest plant in the world to electrically purify salt water has gone on stream at Bahrain in the Persian Gulf.

The Bahrain Petroleum Co., Ltd., a member company of the Caltex Group, installed the plant to produce 86,400 gallons per day of fresh water to supply the drinking and cooking water needs of a community of about 5000 persons centered in Awali near the Bapco refinery, one of the world's largest.

The desalting plant was manufactured by Ionics, Inc., Cambridge, Mass., which developed the desalting apparatus from its basic knowledge of ion exchange and ion transfer. Installation of the plant followed the successful operation of a smaller plant installed on Bahrain more than a year ago.

Other small Ionics plants are in operation in Montana, New Mexico, Texas and on the "Texas Towers" off the northeast coast of the United States. A plant for use in the Neutral Zone between Kuwait and Saudi Arabia will go into operation this year.

The new plant at Bahrain releases, for other uses, distillation equipment which has served the community water needs in the past.

Input water for the Bahrain plant comes from wells drilled on the island. The wells are within sight of the Persian Gulf, but contain only 1/14 as much salt.

The desalting plant is automatic in operation. The principal operating costs are electricity and occasional replacement of thin plastic membranes, of which 4500 are used in the plant. Fifteen kilowatt hours of electricity will make 1000 gallons of fresh water from the feed water. Membrane replacement costs are expected to be less than 50¢ per thousand gallons.

## Meetings of Other Organizations

*1957 Nuclear Congress.*—Peacetime uses of atomic energy will be the topic of the 1957 Nuclear Congress, scheduled for March 11–15 at Philadelphia's Convention Hall, under the coordination of Engineers Joint Council.

Included in the Congress are four major elements, including the Second

## 1956 Directory

The 1956 Directory of Members of the Electrochemical Society is now available. The Directory contains an alphabetical and geographical list of members of the Society as of March 1, 1956, and a list of Patron and Sustaining Members, Past Presidents, and winners of Society prizes and awards.

Members who wish to receive the Directory are requested to fill in and return the order form below, accompanied by check, to Society Headquarters, 216 West 102 St., New York 25, N. Y.

Please send_____ copy(ies) of the 1956 Membership Directory to:

Name_____

Company_____

Street_____

City_____ Zone____ State_____

Attached is check for $_____ for Directory. (Single copies cost $2.00.)

Nuclear Engineering and Science Congress, coordinated by EJC on behalf of twenty engineering and scientific societies. This will include 130 technical papers during a four-day program.

The National Industrial Conference Board will hold its Fifth Conference on Atomic Energy in Industry, featuring 12 round-table discussions.

The International Atomic Exposition, sponsored by the American Institute of Chemical Engineers in cooperation with four other engineering societies, will display industry's latest items in the atomic field.

The Fifth Hot Laboratories and Equipment Conference, sponsored by the Hot Laboratories Committee of the Oak Ridge National Lab., Oak Ridge, Tenn., will take place on March 14 and 15 and deal with the operation and development of equipment for laboratories for atomic energy.

Dr. Walter G. Whitman of Massachusetts Institute of Technology, President of the American Institute of Chemical Engineers and Secretary-General of the United Nations "Atoms For Peace" Conference in Geneva, 1955, is general chairman for the 1957 Congress.

Presented at the Nuclear Engineering and Science Congress will be 130 technical papers dealing with various phases of nuclear operations from mining to the disposal of radioactive waste. Emphasis will be on new developments of potential value to civilian industry, especially in the fields of metallurgy, chemical processing, mechanical, and power application.

Topics which will be covered by the "Fifth Atomic Energy In Industry Conference" are fusion; recent developments in radiation chemistry and radio-isotopes-applications; foreign and domestic markets for atomic energy products; nuclear propulsion; waste disposal; health and safety problems; the economics of new reactor types; the latest developments in atomic energy legislation; site selection problems for nuclear facilities and problems in local and state atomic energy regulations.

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*Chemical Institute of Canada.*—The Chemical Institute of Canada has scheduled the following meetings for 1957.

March 11–13—7th Divisional Conference, Chemical Engineering Subject Div., Kingston, Ont.

May 15–17—Joint Conference, ACS Rubber Div. and CIC Rubber Subject Div., Sheraton-Mt. Royal Hotel, Montreal, Que.

June 3–5—40th Annual Conference, Vancouver, B. C.

October 9–10—Divisional Conference, Biochemistry Subject Div., Ottawa, Ont.

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*Symposium to Describe Nuclear Tests for Nondestructive Testing Applications.*—Nondestructive tests developed in the field of nuclear energy will be the subject of a symposium to be held at the Morrison Hotel, Chicago, Ill., April 16, 17, and 18, 1957. Information resulting from 15 years' research and development in testing applications in the nuclear field will be presented for the benefit of those interested in applying nondestructive test methods to industrial applications. Recently declassified papers will be presented. They will be divided into three categories: (*a*) reactor materials, including fuel, sheath or cladding, control and moderator material; (*b*) completed fuel assemblies; and (*c*) miscellaneous.

Papers will not be available prior to the meeting, but all will be published by the American Society for Testing Materials after presentation.

The symposium is being sponsored jointly by the American Institute of Chemical Engineers, The American Nuclear Society, the American Society for Testing Materials, and the Society for Non-Destructive Testing.

The Chairman of the symposium is W. J. McGonnagle, Argonne National Lab., representing the Society for Non-Destructive Testing.

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*Syracuse Branch, American Electroplaters Society.*—The Third Empire State Regional Meeting will be held April 27 in the Grand Ball Room of the Onondaga Hotel in Syracuse, N. Y.

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*The American Ceramic Society.*—The following meetings have been scheduled for 1957.

May 5–9—59th Annual Meeting, Statler Hilton Hotel, Dallas, Texas.

September 5–6—Structural Clay Products Div., Clemson House, Clemson, S. C.

September 9–10—Basic Science Div., State University of New York College of Ceramics at Alfred University, Alfred, N. Y.

September 26–28—White Wares Div., Materials & Equipment Div., Bedford Springs Hotel, Bedford, Pa.

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*Industrial Nuclear Technology Conference.*—The second annual Industrial Nuclear Technology Conference, sponsored by the Armour Research Foundation of Illinois Institute of Technology and *Nucleonics* Magazine, will be held at the Museum of Science and Industry, Chicago, Ill., May 14–16. For further information write to Dr. Leonard Reiffel, Armour Research Foundation, 10 W. 35 St., Chicago 16, Ill.

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*Symposium on Modern Electrochemical Methods of Analysis.*—This symposium, under the sponsorship of the Section of Physical Chemistry (Commission on Electrochemistry, CITCE, affiliated Commission), and the Section of Analytical Chemistry (Commission on Electrochemical Data), will be held on the occasion of the International Congress of Pure and Applied Chemistry, in Paris, on July 23 and 24. Inquiries should be directed to Professor G. Charlot, Ecole Supérieure de Physique et de Chimie, 10 rue Vauquelin, Paris (V°), France.

## BOOK REVIEW

HANDBUCH DER TECHNISCHEN ELEKTROCHEMIE, edited by Georg Eger. Volume III. Die Technische Elektrolyse Im Schmelzfluss (Commercial Electrolysis of Fused Baths), 2nd Edition. Published by Akademische Verlags., Geest & Portig K. G., Leipzig, 1955. XV + 720 pages, 224 illustrations. Price: DM56 (about $13.50).

It is of interest to electrochemists everywhere to note the reactivation of Engelhardt's Handbuch since World War II, under the editorship of Dr. Georg Eger. Dr. Eger comments on the difficulties encountered in renewing this series after plans were made in 1940 for a continuation. While a completely revised manuscript on the electrolytic production of aluminum was received early in 1943 and others followed, several were destroyed completely during the war, and Dr. Kurt Illig, the author of the chapter on Beryllium, was the victim of an attack. The practice in the field of sodium production changed extensively, and it was necessary to get S. K. Dahl, the director of a Norwegian sodium plant, to revise that chapter.

The new second edition of the volume on Fused Electrolysis is the most comprehensive and up-to-date book on the subject, and was given a favorable review by Dr. Paul Drossbach [*Z.*

*Elektrochem.*, **60**, 523 (1956)]. The new edition is 155 pages longer than the first edition of 1934. Most of this appears in the chapter on Aluminum which is now 307 pages compared to 204 pages previously.

While the new edition has been improved by rearranging the chapters in the order of the importance of the production of the various metals, following a 56-page Theoretical chapter by Dr. H. v. Steinwehr, the chapter headings are the same as those of the first edition and the character of the book has not altered very substantially. A four-page index of firms concerned with fused electrolysis which appeared in the first edition has been dropped entirely for some reason which is not apparent.

While the Theoretical Part was revised throughout, a more detailed treatment, including more recent methods of measuring conductivity and polarization, would be desirable. The second chapter on Aluminum is the most comprehensive in the book, and includes 35 pages of bibliography, covering books, articles, and patents, arranged in chronological and subject classifications. Many photographs of factories and diagrams of plant layouts in the first edition are omitted here, a decided improvement for most purposes. With regard to the processes occurring during electrolysis, Drossbach indicates that there is still much need of revision, and suggests that additional material can be found in the recent books on aluminum production by A. I. Belyaev (Russian) and by W. Fulda and H. Ginsberg (German).

The chapter on Magnesium is much shorter (40 pages) than the one on Aluminum. The chapter in the first edition by P. Camescasse of Paris has been replaced by a similar one by E. Bauer and A. Schmidt of Germany. The bibliography of 57 references to both literature and patents seems brief but well selected. A separate chapter on magnesium alloys by H. Vosskühler follows. This seems relatively much better than the few pages devoted to Alloying Theory in the aluminum chapter.

The chapter on Calcium, Strontium, and Barium is a revision of the original chapter by V. Makow of Paris, by a German (G. Gossrau). This chapter is well done and is followed by an extensive bibliography. Most of the details relate to the production of calcium and calcium alloys, since these have the greatest industrial significance.

The alkali metals are covered in good detail by I. J. Moltkehansen and S. K. Dahl. About 90 pages are devoted to various methods of sodium production, followed by three pages on potassium, eleven on lithium, and two on rubidium and cesium. The methods for sodium production include primarily the electrolysis of fused caustic and of sodium chloride, but the recovery from amalgam is also considered. Likewise, the direct electrolytic production of sodium-lead alloy in the manufacture of tetraethyl lead is reviewed.

Beryllium is well covered by K. Illig, H. Fischer, and W. Birett (70 pages). The chapter is particularly valuable for details of the Siemens & Halske process, developed by the authors.

The chapter on Heavy Metals by G. Eger is brief (27 pages), and could well have been amplified in view of the important future developments in prospect in this field. Recent intensive work on titanium is hardly mentioned. The metals covered include iron, manganese, chromium, nickel, cobalt, zinc, cadmium, bismuth, antimony, arsenic, tin, lead, mercury, silver, platinum metals, copper, and miscellaneous metals.

The chapter on cerium metals by H. Suchanek of Vienna is little changed from the first edition, and the comment is made that there has been little change in the production of the pyrophoric alloys with iron, the most important field of consumption.

The final chapter on miscellaneous applications by V. Engelhart and G. Eger comments on the relatively small use made of fused electrolysis in the chemical industry, and reviews the Acker process for caustic production from salt by way of the fused electrolytic production of lead-sodium alloy. The cleaning of metals cathodically in fused baths is also briefly described.

On the whole the book offers an excellent detailed review of the subject which cannot be found elsewhere. Some chapters have been brought up to date much better than others. Two were noted (calcium, cerium) where the principal or only new reference in the list of books was to Mantell's Industrial Electrochemistry. In concluding his review, Drossbach points out that there exists a wide gap between technical electrochemistry and scientific investigation which has not been bridged, and that one-sided investigations of the kinetics of electrode processes, only, result in some neglect of the other problems of electrolysis such as current efficiency, quality of product, multiple electrodes, flow problems, etc.

The reviewer has repeatedly been impressed with the remarkably close analogies between fused bath electrolysis and the electrolysis of aqueous solutions, rather than the differences. It would seem that many of the phenomena are actually the same in spite of the vast difference of temperature usually involved, and that much could be learned by close comparisons of results in the two fields.

G. Dubpernell

### Notice to Members

According to the Constitution of the Society, Article III, Section 9, "Any member delinquent in dues after April 1 of each year shall no longer receive the Society's publication. . . ." Such delinquents will not receive the May issue of the Journal. A reminder notice will be mailed to delinquents about the middle of February and a final notice about the middle of March.

## ANNOUNCEMENTS FROM PUBLISHERS

High Temperature Technology. I. E. Campbell, Editor-in-Chief. Published by John Wiley & Sons, Inc., New York, 1956. xiv + 526 pages, $15.00.

Latest in The Electrochemical Society Series of Monographs, this volume contains contributions from 35 active workers in the fields of preparation, fabrication, testing, and study of materials suitable for use roughly in the temperature range of 1500°–3000°C or even higher. Highlights of research carried out in recent years, with extensive bibliographies, detailed examination of specific examples, many tables of properties, and thorough discussion of methods used in such studies.

Mitgliederverzeichnis 1956 des Vereins Deutscher Eisenhüttenleute. Published by Verlag Stahleisen m.b.H., Düsseldorf. 408 pages + 95 pages of advertising; excellent printing and bound in a flexible cover.

History and description of the activi-

tics of this society, membership directory (there are 62 members in the U. S. A.), lists of pertinent publications.

FEDERAL FUNDS FOR SCIENCE, V. National Science Foundation report. Available from Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. Price: 35 cents.

Fifth report in a series analyzes for 1955-57 the Federal Scientific research and development budgets according to administering agencies, scientific fields, and character of research.

PHOTOCONDUCTIVITY IN LEAD SELENIDE, J. N. Humphrey, Naval Ordnance Lab., May 1955. Report PB 121174,* 105 pages, $2.75.

THE DIELECTRIC PROPERTIES AND MOLECULAR STRUCTURES OF CERTAIN PARTIALLY FLUORINATED ESTERS, J. B. Romans and T. D. Callinan, Naval Research Lab., Aug. 1956. Report PB 121293,* 33 pages, $1.00.

REACTIONS OF ESTERS OF PHOSPHORUS ACIDS WITH METALLIC COMPOUNDS, R. B. Fox and D. L. Venezky, Naval Research Lab., Aug. 1956. Report PB 121210,* 21 pages, 75 cents.

THE OXIDATION OF ACTIVATED CARBONS AT ROOM TEMPERATURE, R. E. Vander Vennen, Naval Research Lab., Aug. 1956. Report PB 121411,* 18 pages, 50 cents.

THE MECHANISM OF INHIBITORS FOR CHAIN REACTIONS, A. T. Ree and K. Yang, University of Utah for Air Force Office of Scientific Research, Jan. 1956. Report PB 121129,* 13 pages, 50 cents.

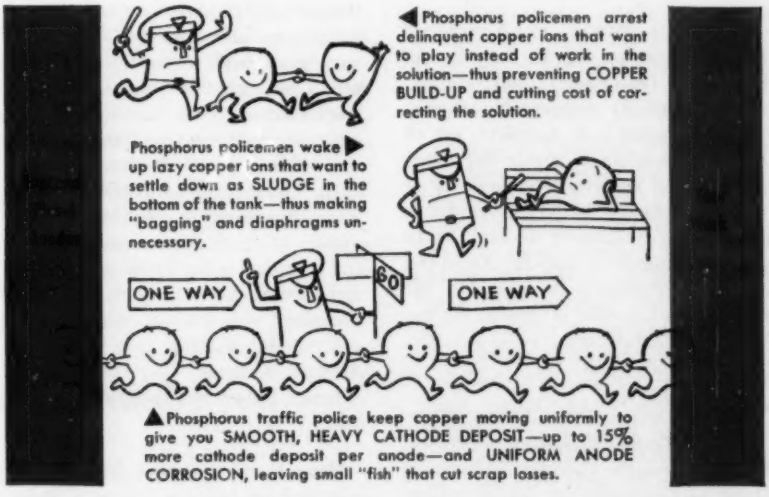
A HANDBOOK OF MAGNESIUM-ORGANIC COMPOUNDS by S. T. Yoffe and A. N. Nesmeyanow, Academy of Sciences, U.S.S.R. Foreword by Professor W. Wardlaw, University of London. Published by Pergamon Press, New York and London. 3 volumes, totaling over 2000 pages; complete $72.00. Exhaustive summary of the vast range of investigations on the organic compounds of magnesium, including the alkyl and aryl halides. All the chemical reactions since Girard (1899) are collected and systematized, together with work described in Russian papers and unavailable thus far. In all, 13,395 reactions are listed, cross indexed, and arranged according to Chemical Abstracts indexing.

*Order from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D.C.

## LITERATURE FROM INDUSTRY

BATTERY-CHARGE CONTROLS. How fully automatic battery charge control enables new Exide Lightguard emergency lighting units to give greater protection against perils of lighting failures with less maintenance than ordinary units is outlined in a new folder, Form 5926. Included is an operation chart demonstrating the reliability of the automatic charge control device. Other charts show beam coverage, light intensity, and protection time. *The Electric Storage Battery Co.*, Exide Industrial Div., Box 8109, Philadelphia 1, Pa.

CORROSION-PROOF VENTILATION AND EXHAUST SYSTEMS. One of the most comprehensive brochures published on the subject of corrosion-proof ventilating and exhaust systems is available. It covers such items as thermoplastic corrosion-proof centrifugal fans, ducting and fittings, and hoods. Of particular interest is the section devoted to a discussion of polyethylene and non-plasticized polyvinyl chloride centrifugal fans. *American Agile Corp.*, P. O. Box 168, Bedford, Ohio.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**To receive further information on any New Product or Literature from Industry listed write directly to the company at the address given in each item.**

HAVEG CORROSION-RESISTANT EQUIPMENT. New 32-page catalogue, C-14, covers the corrosion-resistant plastic equipment of Haveg Industries. Complete coverage is given to the wide range of synthetic resin formulations as well as the newer products and materials. Also included are data on chemical-resistant cements, the field construction of plastic equipment, and Haveg's design service. *Haveg Industries, Inc.*, 900 Greenbank Rd., Wilmington 8, Del.

"COMPACT POWER BY YARDNEY." New brochure on the Yardney line of Silvercel* (silver-zinc) and Silcad* (silver-cadmium) rechargeable storage batteries includes a complete set of technical data sheets giving the latest physical and electrical specifications of available cells and batteries, varying in size from a fraction of an amp hr to many thousands of amp hr. An application questionnaire is provided for those requiring cells of special design. *Yardney Electric Corp.*, 40-50 Leonard St., New York 13, N. Y.

"DIE CASTING WITH ZINC BASE ALLOYS." Technical booklet presents a wealth of specific operating details on those requirements of alloys which affect the properties, mechanical and physical, of the casting produced. It discusses the factors which influence the production of sound zinc alloy castings. Copies are available in quantities for distribution by plant managers to machine operators. *Henning Bros. & Smith, Inc.*, 91-127 Scott Ave., Brooklyn 37, N. Y.

DOW PRODUCTS CATALOGUE. A new edition of Dow's general product catalogue contains more than 375 basic industrial, agricultural, and pharmaceutical chemicals. Detailed information is given in tabular form for quick, easy reference. Information essential for purchasing agents and technical personnel has been included. The index printed with last year's edition is now an integral part of the catalogue. *The Dow Chemical Co.*, Technical Service and Development, Midland, Mich.

"FRESH WATER FROM SALINE SOURCES." Illustrated bulletin describes the electric membrane method of water demineralization, providing design, performance, and cost data on electric membrane plants ranging in capacity from 2500 to 2,000,000 gal of demineralized water daily, and using input water containing from 1000 to 10,000 ppm of total dissolved solids. *Ionics, Inc.*, 152 Sixth St., Cambridge 42, Mass.

"'DAG' COLLOIDAL DISPERSIONS FOR HIGH-TEMPERATURE LUBRICATION," Bulletin No. 423, contains many brief case histories which describe how 'dag' Colloidal Graphite, a high-purity electric-furnace graphite processed to colloidal size and dispersed in a wide variety of fluid carriers, is effectively used for general high-temperature lubrication of oven conveyor chains, kiln car wheel bearings, and virtually any other type of mechanical equipment. Also discussed are applications for 'dag' dispersions of Molybdenum Disulfide. Methods for increasing die life and obtaining better finish at less cost in such operations as forging, extrusion, stamping, wire-drawing, deep-drawing, and stretch-forming are presented. *Acheson Colloids Co.*, Division of Acheson Industries, Inc., Port Huron, Mich.

HIGH VACUUM PUMPS. The recently increased performance ratings of Stokes rotary mechanical vacuum pumps, as well as a wealth of other useful information, are contained in a completely revised edition of the 28-page catalogue "Stokes Microvac Pumps for High Vacuum." The new catalogue, No. 732, includes, in addition to specifications for the complete line of Stokes pumps, valuable tables of formulas, constants and conversion factors frequently used in vacuum processing; solutions to problems of pump selection for typical vacuum systems; and data on continuous oil purification and other maintenance procedures for high vacuum pumps. *F. J. Stokes Corp.*, 5500 Tabor Rd., Philadelphia 20, Pa.

"TECHNICAL REPORT ON HIGH FREQUENCY GAS DISCHARGE PROCESS FOR CHEMICAL SYNTHESES" is available. The Lord Co. has carried out research for several years on the feasibility of synthesis in the vapor phase by r.f. discharge (ca. 27 megacycles) at low pressures, various temperatures, and flow rates. Under semi-pilot plant conditions they claim a conversion efficiency of ammonia to hydrazine of nearly 2% by weight, which they believe to be near commercial possibility. U. S. Pat. No. 2,684,329, issued to A. L. Rouy in 1954, covers early phases of the gas discharge work. *Lord Manufacturing Co.*, Mr. Russell E. Ricketts, 1635 West 12th St., Erie, Pa.

"EVALUATING TITANIUM ALLOYS BY X-RAY DIFFRACTION." New bulletin, reprinted from a national trade publication, describes how Boeing Airplane Co. uses x-ray diffraction to analyze titanium and other alloys. It describes specimen preparation and results obtained with three x-ray techniques: powder camera, diffractometer, and

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spectrograph. In addition to titanium, it discusses such metals as 17-7PH, 303, 321, and 347 stainless steels; 24S, 75S, and 78S aluminum alloys; nickel-chrome salt pot electrodes; and lead-tin solders. *North American Philips Co., Inc.*, Instruments Division, 750 So. Fulton Ave., Mount Vernon, N. Y.

## NEW PRODUCTS

TEMCO FLASK HEATER. A new line of Temco flask heaters has been announced. The same flask heater can be used for several different sizes of flasks. Model 500 will accommodate flasks of 250, 300, and 500 ml in both round and flat bottom. Model 2000 holds both 1000 and 2000 ml flasks. Both models have a top temperature of approximately 1000°F. The flask is cradled in a corrosion-resistant Monel mesh basket suspended within a heating chamber. *Thermo Electric Mfg. Co.*, 545 Huff St., Dubuque, Iowa.

STAINLESS STEEL TEMPERATURE REGULATOR, designed to withstand the corrosive effects of certain fumes, gases, acids, and chemicals, is offered. The regulator, No. 11061-R, was developed mainly for use in chemical plants. Other applications are in plating rooms and in processes where ammonia vapors are present; also recommended for exposed locations. Available in sizes from ¼ in. to 4 in., and in temperature ranges between 20° and 455°F. Requires no external power source. *Robertshaw-Fulton Controls Co.*, Fulton Sylphon Div., Box 400, Knoxville, Tenn.

VACUUM PUMPS. A new line of fast, Roots-type vacuum pumps is available in six standard sizes, covering maximum speed ranges from 92 to 4900 ft³/min. Featuring quiet, vibration-free operation and low power consumption, the pumps have motors which operate within the vacuum, eliminating the need for shaft seals. Heraeus of Hanau, Germany, manufacturer of the pumps, has licensed Consolidated Electrodynamics Corp. as exclusive agent in the U. S. for all models. Further information appears in Bulletin P-8-20. *Consolidated Electrodynamics Corp.*, Rochester Div., 1775 Mt. Read Blvd., Rochester 3, N. Y.

MOBILE COATING UNIT. A new concept in corrosion-resistant coating, a mobile, dual-purpose unit that provides both spray and dip or fluidized coating, has been introduced. The unit, known as the Mark III, consists of a metal reservoir hopper, 15 in. in diameter, 24 in. deep in the powder bed, with an over-all height of 33½ in., and with a maximum width dimension of 20 in. The fluidizing process offers greater flexibility since, in addition to polyethylene, nylon and fluorocarbons can be utilized. *American Agile Corp.*, P. O. Box 168, Bedford, Ohio.

LATEX GLOVES. The velvety "Sueded" inner finish on these gloves curtails perspiration and makes them easier to pull on and off; hence longer wear. Sure Grip Exclusive Crepe outer finish makes slippery and soapy objects easy to hold. Comfortably curved fingers and roomy palm make for better fit and feel. Sizes: small, medium, large, or give glove size. Imported from England. $1.19, postpaid. *Fineline Co.*, 303 Fifth Ave., New York 16, N. Y.

ZINC AND CADMIUM BRIGHTENERS. Two new brighteners have been developed: (*a*) ARP #52, a zinc barrel brightener addition agent that provides a uniform lustrous deposit at lower cost and (*b*) ARP #41, a brightener addition agent for cadmium that produces improved luster at less cost. ARP #52 Zinc Plating Brightener is a powder, available in 10, 50, and 100 lb fiber drums. ARP #41 Cadmium Plate Brightener is a liquid, available in 5-gal pails. *Allied Research Products, Inc.*, 4004-06 East Monument St., Baltimore 5, Md.

FLUORESCENCE ANALYSIS CABINET. A compact fluorescence analysis cabinet, called the Mineralab, for rapid, positive identification under ultraviolet light has been introduced. More than 3000 substances can be activated by invisible ultraviolet energy to emit their own unique glow or fluorescence and can thus be identified, compared, or inspected. Some materials are naturally fluorescent; others can be made so by the addition of tracer dyes or pigments in minute percentages. *Ultra-Violet Products, Inc.*, 5114 Walnut Grove Ave., San Gabriel, Calif.

LAB-CREST STOPCOCK. Fischer & Porter Co. has developed a new stopcock which requires no stopcock grease. The customary glass plug has been replaced by a precision-machined Teflon plug. The unique, self-lubricating property


## CORROSION RESEARCH

For "pioneering" studies on corrosion of unique ceramic materials offering promise for both chemical and metallurgical uses, together with studies on corrosion of zirconium and its alloys. Will include not only aqueous solutions but also fused salts and metals. Experience in corrosion testing helpful but not essential; degree in chemistry, physical chemistry, metallurgy, or chemical engineering desired. Right young man can grow into position of responsibility in expanding R&D program on materials for nuclear energy. *Write to:*

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**THE CARBORUNDUM COMPANY**
**NIAGARA FALLS, NEW YORK**

of the Teflon provides "nonfreezing" operation while maintaining a leakproof seal. *Fischer & Porter Co.*, Glass Div., Hatboro, Pa.

VYTHENE. New solvent called Vythene is a noninflammable trichloroethane which has solvent properties similar to carbon tetrachloride but a far lower toxicity. The maximum allowable concentration in air is 500 ppm, about 20 times as great as that of carbon tetrachloride. It is pleasant in odor and boils at a slightly lower temperature than carbon tetrachloride. Available in 5-gal drums. *Chicago Apparatus Co.*, 1735 No. Ashland Ave., Chicago, Ill.

YARDNEY SILVERCELS.* Two new models, designated as the LR 200 and the LR 300, are the latest additions to the Yardney Silvercel® line. The largest commercial silver-zinc production cell in the world, the LR 300 has a capacity of 300 amp-hr at a nominal voltage of 1.5 v. It weighs 9 lb, 4 oz when filled and has an over-all volume of 82 in.$^3$. The LR 200 has a nominal capacity of 200 amp-hr, a filled weight of 6 lb, 6¼ oz, and is applicable to both medium and low rate applications. Complete electrical and physical characteristics available. *Yardney Electric Corp.*, 40-50 Leonard St., New York 13, N. Y.

* Trade Mark

## EMPLOYMENT SITUATIONS

Please address replies to box shown, c/o The Electrochemical Society, Inc., 216 W. 102nd St., New York 25, N. Y.

### Position Wanted

BATTERY ENGINEER, 37–17 years' experience in lead acid batteries. Capable of setting up and operating battery testing laboratory for production, research, and military test programs. Experienced in all types of Government and special purpose batteries, including aircraft. Knowledge of latest production methods of dry charging, formation, and oxide manufacture, mixing, and pasting. Complete resume will be supplied on request. *Reply to Box 360.*

### Positions Available

METALLURGIST. Company engaged in extractive and pyrometallurgy requires a man for production and development, preferably with experience in one or more of the following: smelting and refining, steelmaking, or electric furnace operation. Excellent opportunities for qualified man. All replies strictly confidential. Submit detailed resume, including educational and employment backgrounds, as well as salary requirements, to *Box A-269.*

ELECTRONIC SCIENTISTS, METALLURGISTS, PHYSICISTS, TECHNOLOGISTS, AND ENGINEERS (Aeronautical, Electrical, Electronic, Industrial, General, Mechanical, and Power Plant). The Naval Air Material Center, Philadelphia 12, Pa., has an urgent need for qualified engineering and scientific personnel to fill vacancies in the above positions. The Center is currently engaged in an extensive program of aeronautical research, development, experimentation, and test operations for the advancement of Naval aviation. Starting salaries ra from $4480 to $7570 per annum. Ap cation for Federal Employment, Sta ard Form 57, should be filed with Industrial Relations Dept., Naval Material Center, Naval Base, Phil delphia 12, Pa. Applications may obtained from the above address or formation as to where they are availab may be obtained from any first second class post office.


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# Electrochemists Experienced in Secondary Battery Research and Development

Long established U. S. electrochemical company is expanding its product line to include smaller sizes of storage batteries. Plans to augment present Research and Development staff in Midwest with men of outstanding scientific training and ability and having several years experience in this field. Applicants should have thorough basic knowledge of secondary systems, including nickel-cadmium.

Pleasant working conditions with scientists and engineers of similar training on scientifically challenging new applications of secondary battery power. Imaginative man preferred.

Company provides full benefit plans and salary commensurate with experience.

Please send details of your background and experience. All information held in confidence.

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